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AMERICAN

CHEMICAL JOURNAL

EDITED BY

IRA REMSEN

PRESIDENT OF THE JOHNS HOPKINS UNIVERSITY

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AMERICAN CHEMICAL JOURNAL

THE OSMOTIC PRESSURE AND THE DEPRESSION OF THE FREEZING POINTS OF SOLUTIONS OF GLUCOSE.¹

BY H. N. MORSE, J. C. W. FRAZER AND B. S. HOPKINS.

PART I.²

In a previous communication³ we described certain "thermometer effects," or "temporary fluctuations of pressure which follow changes of temperature and are due to the expansion or contraction of the liquids in the cell, and not to actual variations in osmotic pressure," and we announced our intention of eliminating these troublesome phenomena by working, in the future, at constant temperatures, or at temperatures so nearly constant that the passage of water through the membrane can keep pace with the expansion and contraction of the contents of the cell.

¹ The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution.

² Our measurements of the osmotic pressure of solutions of glucose are not yet as numerous as we desire to make them before publishing the results, the work having been delayed by difficulties, some of which are explained in the present paper. The reason for dividing the account of the work and publishing the first part at the present time is a desire, on our part, to make clear, without unnecessary repetition, the conditions under which another investigation was prosecuted, namely, *the redetermination of the osmotic pressure of cane sugar solutions*, an account of which is given in the following paper.

³ THIS JOURNAL, 34, 23, 92.

These "thermometer effects" were the most serious obstacles with which we had to contend in our attempt to secure accuracy in the measurement of pressure, and the means which we have since employed to reduce them to harmless proportions are quite elaborate. In general they consist of: (1) A large and well protected bath containing over 300 liters of water, which is kept in constant motion; (2) a nearly tight enclosure over the bath, the air in which is kept in constant circulation through pipes lying in the water below; and (3) various automatically regulated electric and gas stoves, which serve to maintain uniform temperature conditions outside the bath.

The bath is a rectangular wooden box 1.23 meters in length, 0.45 meter in width and 0.65 meter in depth which is lined with copper. Its total capacity is 360 liters, while the space occupied by the water is about 300 liters. This tank, or bath, is surrounded by a larger wooden box of such dimensions that the distance between them is not less than 75 mm. at any point, and the intervening space is tightly packed with hair.

The house above the tank has a height of 0.5 meter, a width equal to, and a length about three-fourths, that of the bath. It is provided with a top, or cover, which is hinged at the back, and is opened or closed by means of a cord running over stationary pulleys on the ceiling above. It is also provided in front with a mirror plate-glass window, which is hinged at the bottom. The bath, with the house above, rests upon heavy brackets, which are built into the thickest and most stable of the masonry walls of the laboratory. The same is true of the cathetometer and the standard scale which are employed in the measurements. These instruments, like the bath itself, rest upon supports which are independent of the floor or other woodwork of the building.

The cells, when a measurement is in progress, are located in the bath at a depth considerably below the surface of the water, while the portions of the ascending limbs of the manometers which contain the air are in the house above. Hence the liquids in the cell tend to take the temperature of the

water, and the gas in the manometers, the temperature of the air above. It is, therefore, important (1) that the temperature of the water and of the air within shall be kept nearly constant, and (2) that the temperature of the air shall not differ greatly from that of the water.

Since the trustworthiness of our results is measured solely by the excellence of the method by which they were obtained, and nothing should be taken for granted on that score, we shall not hesitate to describe the details of our present arrangements. These details are seen in the accompanying figures.

Fig. I. is a longitudinal section through the middle of the

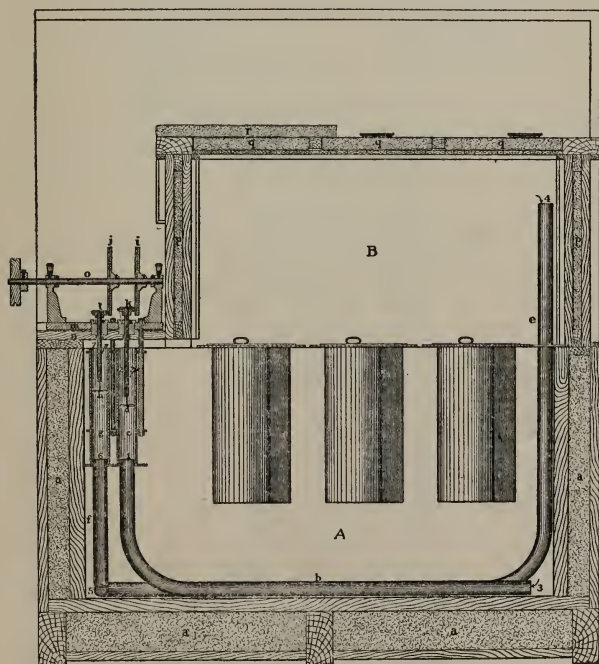


Fig. I.

bath. A is the water tank and B the house, covering about three-fourths of it. The hair packing between the tank and the box is designated by the letter *a*. The lead pipe *b* (see also Fig. II.), which has an internal diameter of 30 mm., lies upon the bottom of the tank and enters the larger brass pipe *c* at 1. The brass pipe *c* is provided with a series of holes extending entirely around it at 2, Fig. 1A, which is below the

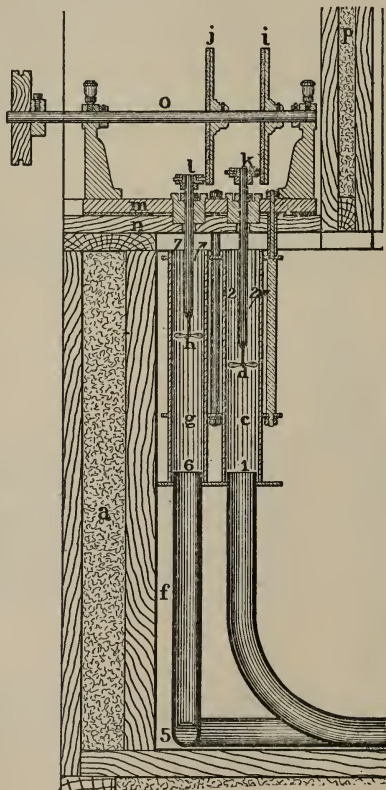


Fig. 1A.

level of the water in the tank. By means of the propeller *d*, the water is constantly drawn into the lead pipe at 3 and delivered through the holes at 2 in the brass pipe. In this manner, with the propeller running at a moderate rate, a uniform temperature is secured throughout the whole body of the water, so uniform, in fact, that differences cannot be detected with the thermometers graduated to $0^{\circ}.1$.

The two lead pipes, through which the air in the house above the tank is drawn, are of the same size as that through which the water is pumped. One of these, *e* Fig. I. (see also Fig. II.), is shown in the background. Starting at 4, at the rear right-hand corner, it passes downwards through the water and then along the angle made by the bottom and back of the tank to the other end, where it curves and enters the vertical pipe *f* at 5. At this point it meets the other air pipe *e'* (see Fig. II.), which is identical with it except that the latter occupies the opposite side of the bath. The vertical pipe *f*, which serves as a junction for the two air pipes *e* and *e'*, like the water pipe, enters a larger brass pipe *g* at 6, which extends to some distance above the surface of the water. By means of the rotating fan *h*, the warmer air in the upper part of the house is constantly drawn through the pipes *e* and *e'*, lying in the water, and is delivered again at 7 above the surface at the other end of the tank. The air in the house is thus kept in circulation, and at a uniform temperature which cannot rise much above, or fall much below, that of the water in the bath. The magnitude of the difference between the temperature of the air and that of the water will depend, of course, upon the rapidity of the circulation of the former through the submerged pipes, *i. e.*, upon the efficiency and speed of the fan, also upon the tightness of the house and the frequency of opening it for the purpose of introducing or removing cells.

The machinery by which the pump *d* and the fan *h* are rotated is located above the tank at the left (see Fig. IA), and outside the house. It consists, essentially, of the two rotating disks *i* and *j*, which drive the pump and fan pulleys *k* and *l*. Both the disks and the pulleys are faced with sole leather, and the facings of the former are so trimmed on the

lathe that they increase slightly in thickness from the center outward. The advantage of giving this form to the disk face is obvious. The friction between it and the pulley remains constant, since any wearing away of the running surfaces is automatically compensated by a drop of the pulley. The speed of the pumps can be regulated at will, within large limits, by adjusting the pulleys to run at different distances from the centers of the disks. The gradual descent of the pulleys to compensate for wear is attended by an increase of speed, but the effect is small since the drop does not amount to more than 1 mm. per month of constant running. The iron bed plate *m* is raised above the wooden tank cover *n* by thick strips of asbestos board, thus providing for ventilation. A further precaution against communicating to the bath the small amount of heat developed by the machinery consists in placing two small fans (not shown in the figure) upon the shaft just above the pulleys.

In the first bath built by us, the air compartment covered the whole tank, and the disks and pumps were inside and the motor and driving pulley outside the house. This arrangement was, however, found to be a bad one, owing to the high speed which had to be given to the fan in order to keep the temperature of the air near that of the water.

As now arranged, the machinery runs smoothly and with little noise. The heat developed by it does not sensibly affect the temperature of the bath. The air-fan is made to rotate about 2500 times per minute, and the water pump about 800 times.

It is essential in a bath of this kind that the enclosure above the water shall be as nearly air-tight as it is possible to make it. This condition has been realized in our apparatus to a satisfactory degree by selecting thoroughly seasoned lumber for its construction, by setting all tongues of the woodwork in their grooves with an elastic varnish, by embedding strips of insulating tape in varnish over all joints, and, finally by enameling heavily the whole interior of the house. The hinged top and the plate-glass window in front close, at all points on the inside, against rubber weather strips, and the cracks upon

the outside are covered with strips of insulating tape, which is usually sticky enough to adhere firmly to the wood, but is easily removed whenever the bath is to be opened at the top or in front.

The house, as well as the tank, has double walls, except in front and on the top, and the spaces between the walls are filled with hair as seen at *p* in Fig. I. The spaces in the framework of the top *q, q, q*, are filled with hair, which is held in place by a covering of flannel tacked to the frame. Finally, the whole top of the house is covered by the hair mattress *r*. The glass of the window in front is completely covered by a thick flannel-encased pad of hair, which is divided at various points, from the upper edge towards the bottom, thus providing numerous narrow curtains, any one of which may be lowered for the purpose of reading a manometer or thermometer without exposing more than a very small portion of the glass of the window, the light necessary for the illumination of the instrument being thrown in from the outside.

However great the fluctuations of temperature outside the bath, the changes in the temperature of the large body of water within are necessarily very slow. The effect of external conditions upon the temperature of the enclosed air space is more marked. A considerable rise or fall on the outside is soon followed by a small corresponding change in the temperature of the air above the water, but such fluctuations are not large or of long duration, even under the most unfavorable conditions, owing to the continuous and rapid circulation of the air through the submerged pipes. The rate of this circulation can, of course, be increased, if desired, by raising the speed of the fan.

Fig. II. presents a view of the tank as seen from above, and serves to explain the internal arrangements for the accommodation of the cells and also some of the features of construction which have already been pointed out.

The water and air pipes are seen, the former at *b* and the latter at *e* and *e'*. The hair packing between the tank and the exterior box is designated at various places by the letter *a*.

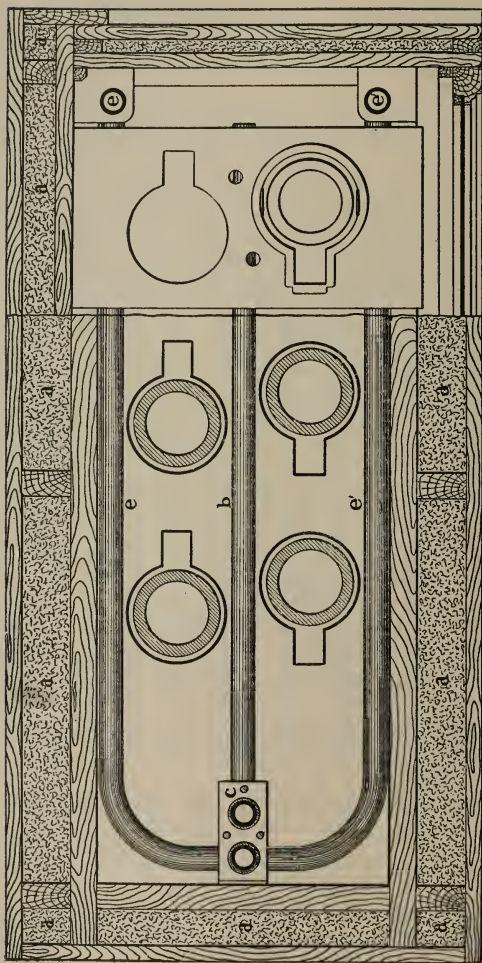


Fig. II.

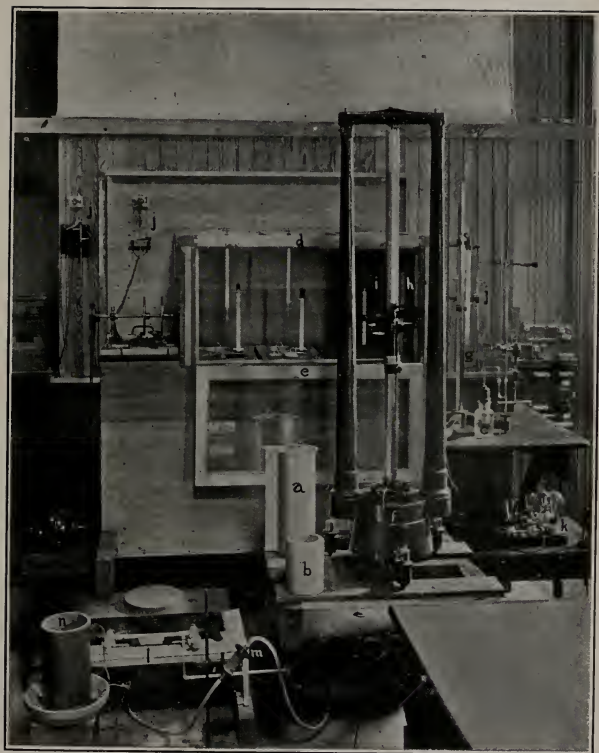


Fig. III.

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There is also seen at the right in Fig II. one of the three iron plates which rest upon the edges of the tank (see also Fig. III.) and serve to hold in place the six galvanized iron cans (*a* Fig. III.), in one of which the cell is placed when a measurement is to be made. Each plate is perforated for the reception of thermometers, which give the temperature of the water in the bath.

The cans, *a* Fig. III., have a depth of 0.4 meter and a width of 0.15 meter, and are provided on one side with a rectangular extension for the accommodation of the long vertical limbs of the manometers. To weight the cans in the water, and at the same time to facilitate an even distribution of heat, heavy cast-iron cylinders (*b* Fig. III.) are employed. These cylinders, weighing each about 8 kilograms, are placed in the cans, and the bottles containing the cells rest upon the bottoms of the latter within the former. The can *a*, the iron cylinder *b* and the bottle for the cell are seen in their respective positions and correct relative proportions in Fig. IV. The open end of the can is plugged with hair while a measurement of pressure is in progress, in order that the cell contents may more surely acquire the temperature of the water, and the air in the manometer that of the house above.

Fig. III. is a photograph of the bath in an unfinished condition, together with certain accessories which will be described later. The hinged cover of the bath, stripped of its upholstery, is shown at *d*, *e* is the plate-glass window without its curtain, *f* is the cathetometer, and *g* the standard scale. Within the bath are seen parts of the vertical portions of the air pipes (*i* and *h*), the iron plates, the upper ends of some of the cans, and the usual arrangement of the thermometers; while to the left, on the outside, is shown the machinery by which the water and air pumps are driven. It is to be stated with regard to the thermometers used in the bath that they are all graduated to $0^{\circ}.2$, and that the errors of each have been determined by comparison with a thermometer which has been tested at the "Reichsanstalt."

The only remaining feature of the bath which requires explanation is the automatically regulated electric stove, which

was devised for the purpose of raising and maintaining the

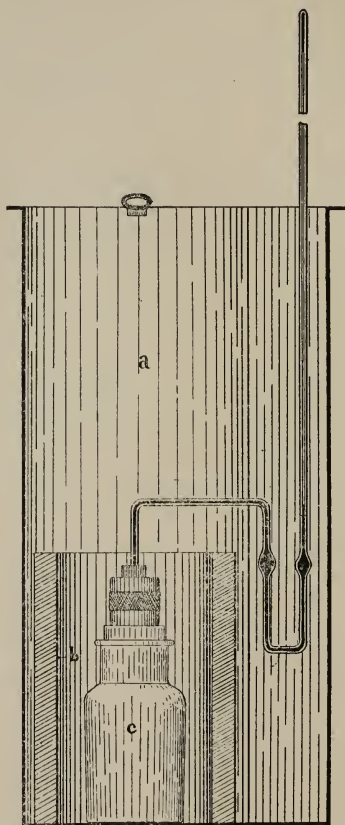


Fig. IV.

temperature of the water whenever it is desired to secure measurements of pressure at higher temperatures than those

prevailing outside the bath. The stove in question is shown in Fig. V. It consists of the porcelain tube *a*, which has a

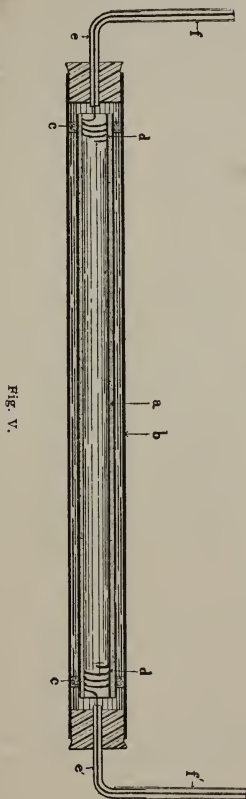


Fig. V.

length of 625 mm. and a diameter of 30 mm. and the enamelled steel tube *b*, which is separated from *a* by the asbestos rings *c*, *c*. The ends of the porcelain tube are silvered for a

short distance, both externally and internally, and the outside is graphited by the method previously described by Morse and Frazer.¹ Electrical contact is secured by the expanding spring wire coils d, d , which are inserted in the ends of the porcelain tube and press against the silver lining. The ends of the steel tube are closed with rubber stoppers, through which pass the short bent glass tubes e, e' . The leads to the battery are protected from the water by the rubber tubes f, f , which fit the wires so loosely that air can readily pass in either direction. The stove lies on the bottom of the tank, with the leads extending upwards through the water and out of the bath at one end. It is connected with a 74-volt battery and yields, with no external resistance in the circuit, and at about 20° , 50,000 calories per hour. When the stove is in use it is necessary to give the pumps a somewhat higher speed than is otherwise required in order to secure uniform temperature conditions. The stove circuit passes through a relay which is automatically operated by a sensitive thermostat placed in the water of the bath. The thermostat will be described later. We have had, up to the present time, but little occasion to use the bath stove because most of our measurements have been at temperatures which could be secured and maintained without its aid.

With a bath so well protected and containing so large a body of water, and capable, therefore, of absorbing or yielding up so much heat without any great change of temperature, we should have accomplished our object—the *elimination of thermometer effects*—had it not been for the fact that our building is heated only during the working hours of the day, *i. e.*, about 8 hours in the 24. The variations of temperature outside the bath were, accordingly, large, amounting frequently, in the winter months, to 25° . Even with so wide differences in the external conditions, the temperature changes in the water were very slow. These changes were twofold and characteristic. They consisted in a slight rise, during the daytime, above what may be called an equilibrium temperature, and a slight fall below it at night, and, at the same time, a slow but

¹ THIS JOURNAL, 32, 93.

continuous change in the temperature of the water, which was, in general, upwards or downwards, according to the season.

The effect of the large daily fluctuations of temperature outside the bath upon the temperature of the air within the manometer house was much more marked, and the highest speed of the air pump did not suffice to reduce the temperature differences of water and air to what we considered tolerable limits. Hence measures were taken to secure more uniform temperature conditions in the room in which the bath is located, and, since some of the appliances which were devised for this purpose are of a generally useful character, we shall describe them.

First of all, the bath was enclosed by a structure—3.3 meters in length, 2 meters in width, and 2.6 meters in height—which consists of a wooden framework, covered on both sides with thick muslin. The cloth upon the vertical walls was sized with gelatin to render it less pervious to air without interfering too greatly with the light, while that upon the roof was both sized and painted. The distance between the cloth sides is everywhere about 50 mm. The structure is provided with two doors of the same construction as the rest of the walls, also with windows at convenient points, which may be opened for the admission of daylight when it is desired to avoid the heat of electric lamps, *e. g.*, when the calibration of a manometer is in progress.

The space thus enclosed is maintained throughout the night at nearly constant temperature by an electric stove, which is controlled through a relay by means of a thermostat. The stove which is seen at *n* in Fig. III., is a terra cotta cylinder 300 mm. in height and 150 mm. in width. It is graphited externally by the method previously described¹ by Morse and Frazer and develops, when connected with the 74-volt battery, 250,000 calories per hour.

The relay which is used in connection with the stove is seen at *k* in Fig. III. It is of the common "pony" type which is employed on short telegraph lines, with provision, however,

¹ THIS JOURNAL, 32, 93.

for the prevention of sparking when the stove circuit is opened or closed by the thermostat.

The mercury thermostat, which is employed to control the stove circuit, is shown in Fig. VI., and again at *j, j, j* in Fig. III. It is the instrument which we use to control the temperature of all kinds of laboratory baths, whether they are heated by electricity or by gas.

The principal objection to electric mercury thermostats is the sparking which occurs at the closing and, particularly, at the breaking of the circuit. The surface of the mercury and the interior of the glass tube soon become fouled with oxide, and the instrument is thereby rendered unreliable. The practice of covering the end of the mercury column with a layer of non-conducting non-oxygen absorbing oil is an unsatisfactory remedy because it results, especially in sensitive thermostats, *i. e.*, in those having narrow tubes, in a breaking of the column. The method of preventing sparking which we employ, and which we have found to be quite effective, consists in spanning the spark gap with a resistance which has a certain relation to the potential of the battery.

Fig. VI. represents the thermostat. It resembles the Reichardt thermostat for gas, and most of the electric thermostats which we have in use in the laboratory are, in fact, transformed Reichardt instruments. The brass rod *a* passes through the cork and is terminated by a platinum tip. It is connected through the wire *c* with the binding post *b*, which, in turn, is connected with the resistance *R* by the wire *d* and with the coils of the relay by the wire *e*. The adjusting screw *f*, on the other hand, is connected by the wire *h* with the binding post *g*, which is connected, in its turn, with the resistance *R* by *i*, and with the battery by *j*. The coil spring of brass wire *k*, by pressing the screw *f* outward, gives a surer electrical connection and a more permanent adjustment of the mercury. It also tends to prevent leakage of mercury along the screw thread.

For use in a room, or any other large space where the whole of the thermostat is within the enclosure, the instrument, including binding posts and resistance, is mounted on a board

which may be attached by screws to the wall or to any other

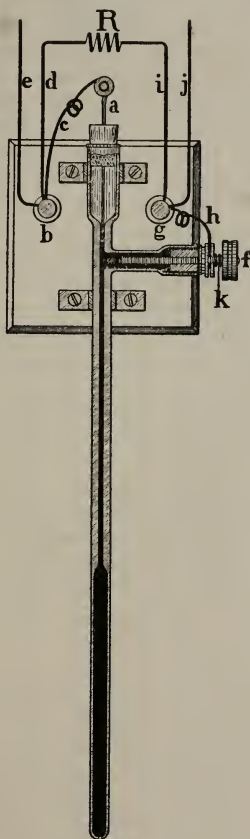


Fig. VI.

suitably located permanent object. If, on the other hand, only

the bulb of the instrument is to be immersed, as in a water or ordinary hot-air bath, the binding posts *b* and *g* are screwed into a small wooden block, which is bored through the center and firmly attached to the stem just under the side tube. Obviously, if a close regulation of temperature is required, in cases where only the bulb of the thermostat is within the heated space, the capacity of the side tube should be very small as compared with that of the bulb. This important point is usually overlooked by the makers of such instruments.

The relation of the resistance *R* to the potential of the battery requires careful attention. We use with each thermostat a single portable storage cell. The potential is, therefore, about 2 volts at all times, and the resistance, which wholly suppresses sparking in our instruments, is 200 ohms. This is just about the resistance of the *cold* filament of a 75-volt 16 candle-power lamp. Accordingly, a lamp of that rating is inserted in the shunt around the spark gap. With this relation of resistance to potential no sparking can be observed and the thermostats, if the mercury is pure and properly protected against dust, give satisfactory continuous service for several months without cleansing.

Since the circuit through the shunt is always closed, this method of suppressing sparking involves a waste of current while the circuit through the thermostat is open, but the loss amounts to only about 0.01 ampere and is quite insignificant.

The same device is employed to diminish sparking in the relay. The gap is shunted through lamps. Owing, however, to the comparatively high pressure of the battery for the stove, it is impracticable wholly to suppress the sparking, though it can readily be reduced to a tolerable limit, *e. g.*, to that which is usually observed in a relay on a telegraph line. The fraction of the current which flows continuously around the spark gap of the relay is not wasted, as in the case of the thermostat, because it necessarily contributes its proportion to the heat which is required to maintain the temperature of the room. It is hardly necessary to state that, in preparing a relay for use in a stove circuit, the usual position of the stops of the instrument must be reversed.

During the cold weather of the winter, the tax upon the battery which was necessary in order to maintain the temperature of the enclosure about the bath was inconveniently heavy. Accordingly, we determined to aid the electric stove by heating the outer room at night with a gas stove; and it was desirable that the latter, like the former, should be subjected to automatic regulation. The outcome was an electric gas regulator, controlled by an electric thermostat, which proved so satisfactory that we now use it for all kinds of baths heated by gas.

The gas stove is seen at *l* in Fig. III. Its construction is sufficiently obvious, and the only points to which attention will be called are the steel plate covering the stove and the cast-iron disk resting upon it. The former serves to protect the flames from air draughts, and the latter, to moderate—by continuing to radiate surplus heat, the fall of temperature which succeeds the partial shutting off of the gas supply. Only one of these disks is shown in the figure, but in cold weather a larger number of them can be employed with advantage.

The thermostat which is used to control the gas supply differs in no respect from that which is employed to regulate the electric stove. It is placed beside the thermometer, which is located, of course, with a view to ascertaining, as nearly as possible, the mean of the temperature conditions of the room.

The gas regulator is seen at *m* in Fig. III., and in Fig. VII. The soft iron tube *a*, Fig. VII., serves as a magnet core to raise and release the iron ball *b*, and thus to control the flow of gas through the regulator in the direction of the arrows. The ends of the core are slightly countersunk to furnish a seat for the ball, and the flaring sides of the openings are grooved to provide passages for a small amount of gas around the ball when it is in its place at the end of the tube. The brass tube *c* has an internal diameter quite exactly equal to that of the ball, so that the latter is always correctly guided to its proper position when the circuit through the coils of the magnet is closed by the thermostat. The internal wall of *c* is grooved longitudinally to a depth which will permit an abundant sup-

ply of gas to pass the ball. The ball rests upon the open brass wire spring *d*, which may, with advantage, have a considerable length and should not be made of very stiff wire. The

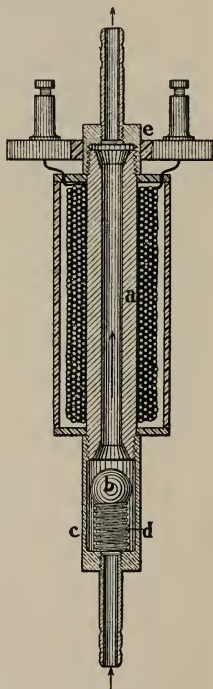


Fig. VII.

other end of the core is furnished with the brass tube *e*, which is shorter than *c* and not grooved internally; *c* and *e* are interchangeable.

The winding of the magnet should, of course, be with refer-

ence to securing the longest life for the battery which is consistent with the efficient working of the instrument. All of our magnets are wound to a resistance of 20 ohms, and the portable storage cells which are used with them have a capacity of 50 ampere hours; accordingly, a single charge of a cell should suffice—excluding unavoidable waste—for 500 hours' continuous use of a regulator. But, since the discharge is intermittent, the endurance of the cell may be greater. Having determined what resistance a magnet is to have, the selection of the size of the wire to be used will, of course, depend on the manner of winding, *i. e.*, whether a single wire or several in parallel are to be employed. In any case the result sought will be to secure the largest number of turns in close proximity to the core which is consistent with the limiting conditions.

The circuit through the shunt to the spark gap in the thermostat is always closed, but, since this circuit also includes the magnet, its resistance is not less than 220 ohms, and the waste of current is therefore small.

Considered simply as a magnet and from the standpoint of efficiency, the regulator here described has obvious defects, but in order to utilize more fully than we have done the magnetic effects, it would be necessary to construct a much more complex and costly instrument.

The gas regulator, the battery, and the thermostat are connected in series, and, in order to reduce to a minimum the work to be done by the magnet, the regulator is fixed in an inclined position, as shown in Fig. III. The inclination given to it is such that the highest pressure of the gas (aided by the spring and the slightly magnetized condition of the core, which is due to the small current flowing continuously through the thermostat and magnet coils) will not quite suffice to raise the ball.

The arrangements for the regulation of temperature, which because of the importance of their purpose have been described at length in the foregoing pages, have been found entirely adequate. The "*thermometer effects*," which gave us so much concern while engaged in the measurement of the os-

otic pressure of cane sugar solutions, do not, under present conditions, manifest themselves.

It may be of interest to know within what limits the various appliances are effective, and these can be stated with a fair degree of precision. The temperatures of the larger room, which is heated by gas, and of the smaller one, which is heated by electricity, are recorded at regular intervals four times each night by the watchman. The records extend over several months and show fluctuations during the night, in winter, not exceeding 1° in the outer room and $0^{\circ}.5$ in the inner one. The usual fluctuations during the night are less than $0^{\circ}.6$ in the former and $0^{\circ}.25$ in the latter. These statements relate to the temperature at night only. Whatever difficulty we have had in the regulation of temperature has been due to the frequent overheating of the building during the day. The change in the temperature of the water of the bath, which is produced by an occasional overheating of the building, is, however, not sufficiently great or rapid enough to produce sensible thermometer effects in the cells.

Another difficulty which was encountered in our earlier work was the uncertainty regarding the true volume of the upper end of the manometer in the region where the form of the tube is altered in closing it. As stated in the published account¹ of that work, the form at this point was assumed to be spherical or conical according to its appearance, and the errors resulting from such an assumption were probably small except, perhaps, in the case of concentrated solutions. The doubt concerning the exact form of the end was not the only uncertainty introduced by the operation of closing the tube. The heating of the glass may well have been followed by changes of caliber farther down the manometer, as far down, in fact, as the heating effects of the flame extended. These changes of caliber, if they occur, are analogous to those observed in a thermometer bulb after heating, but in the case of a manometer there is no possible way of discovering their magnitude, since the calibration precedes the closing of the instrument.

¹ THIS JOURNAL, 34, 11.

Again, it is often difficult to locate with certainty the upper end of a fine tube, especially when the glass walls are thick and the form of the end is spherical or conical. There is the liability that the point sought will be slightly displaced owing to lack of parallelism between the inner and outer surfaces of the tube, and the fact that the surfaces in the region in question are not perpendicular to the line of vision. After finishing the first series of measurements on cane sugar solutions, we attempted to ascertain how far errors of reading from this source had entered into the work. A fine needle with a sharp point was fixed in a vertical position in the usual place of a manometer, and its length was determined by means of the telescope and the standard scale. The upper end of the manometer was then cut off and the detached tube placed over the needle, after which its length was again determined. The results were reassuring, since we could in no case detect a measurable difference between the length of the naked needle and its apparent length when covered by the tube.

In an earlier communication¹ we stated that Professor Abegg had kindly called our attention to an effective remedy for the uncertainties connected with the form of the closed end of the manometer—that of filling it with mercury, but that we had not, up to that time, succeeded in applying it to our satisfaction, owing to the difficulty of separating from the main column the necessary portion of mercury and of dislodging all the air from the space which it should fill completely. The much desired result has since been accomplished in an easy and entirely satisfactory manner, as follows :

After calibration, and when it is to be filled, the upper open end of the manometer is attached to a two-way stop-cock with one of its passages leading to a supply of mercury and the other to the supply of purified air.² When the air has been drawn into the manometer for the last time, a small quantity of mercury is allowed to follow it and close the tube. If the quantity which has been admitted is too large or too small, it can readily be readjusted by manipulating the reservoir and the stop-

¹ THIS JOURNAL, 34, II.

² *Ibid.*, 34, 9.

cock. The reservoir is then lowered until a large part of the air is in the bulb upon the vertical limb and the mercury plug which imprisons it is at a considerable distance from the top. The upper end of the tube is then drawn out to a finer one with thin walls, and the mercury plug is brought to its place by raising the reservoir, care being taken not to drive it into the narrower portion of the passage. The problem now is to "boil out" the space occupied by the mercury in such a thorough manner that no air will be left between it and the glass, and this is readily accomplished after a little practice. The upper end of the column and the finer tube above are cautiously heated. When the vapor has developed to a certain extent, the whole body of the mercury is driven by the pressure a short distance down the tube. It is immediately brought back and the upper portion of the metal is again heated. After a few repetitions of the procedure, the end of the tube is closed. While closing, it is necessary to have the air in the manometer under somewhat diminished pressure in order that the softened glass may collapse, and the mercury is again driven a short distance down the tube; but on cooling it reascends and fills completely the space in the upper end of the manometer and, ordinarily, no difficulty is thereafter experienced in consequence of its dislodgement or the breaking of the column. The column of mercury in the closed end of the manometer is made considerably longer than would be necessary if only the form of the tube in this region were in doubt. It is made to fill, likewise, all that portion of the tube, lower down, whose caliber may have been altered by heating the glass while closing the instrument.

The manometers which were used in the earlier work were provided with one bulb, which was located on the descending limb of the instrument. The arrangement, however, led to frequent disasters while closing the cells, due to the considerable oscillations of the mercury column during the rather violent manipulation which is necessary for the proper insertion of the manometer stoppers. The air, on such occasions, often escaped from the ascending calibrated limb into the descending one, making necessary an opening and refilling of the instru-

ment. Attention has already been called to this difficulty and the proposed remedy, namely, the blowing of a second bulb near the bottom of the ascending limb. Our present manometers, therefore, have two bulbs, and the one which was more recently introduced serves not only to prevent escape of air while the cell is being closed, but also as a storage place for the air while the operation of closing the manometer in the manner described above is in progress.

A further improvement in manometers, which has served to reduce materially the earlier experimental difficulties, concerns the form of the permanently open end of the instrument, *i. e.*, the end which is submerged in the solution in the cell. The crowding upwards of the manometer under the pressure of the contents of the cell has, from the first, been one of the most persistent of the many troubles which had to be met in the attempt to reduce the measurement of osmotic pressure to a reasonably accurate quantitative basis. The slipping of the manometer in the stopper is attended by a dilution of the solution in the cell, the exact magnitude of which it is impossible to ascertain. If the displacement were limited to the manometer, the extent of the dilution could be quite accurately computed, but it never is so restricted. The material of the rubber stopper is likewise displaced to a greater or smaller extent whenever the manometer is pushed upwards. The exact extent of the upward movement of the manometer is known in every case from the record of the observations taken at the telescope, but it cannot be ascertained how much of this is due to slipping and how much to lack of rigidity in the stopper. Consequently, no entirely safe correction is available for the increase in the capacity of the cell. Hence the endeavor has been, from the beginning, to fix the manometer in the stopper so tightly, and to render the rubber about it so rigid, that the former cannot slip and the latter cannot "bulge." The arrangements which had been made with this end in view were already quite elaborate when the first series of formal measurements of the pressure of cane sugar solutions was undertaken, and they were fully described in the account of that

work. A number of useful changes have, however, since been made which will be explained.

Formerly, a bulb was blown near the open end of the manometer, the idea being that any upward movement of the instrument while in the cell would be quickly arrested through the rapidly increasing resistance of the material of the stopper. The enlargement of the end of the tube has been found indispensable; but the blowing of a bulb in this position produced a cavity which is always necessarily filled with the solution under investigation, and which must, therefore, be emptied and cleansed after each experiment and refilled before the succeeding one. The diameter of the passage into the bulb is, however, only about 0.5 mm., and the withdrawal or introduction of liquids through it by means of fine pipettes is slow and troublesome. Hence the bulb has been replaced by an enlargement of the tube, which is made without increasing its bore, and any solution which is within the manometer can now be expelled by simply inclining the instrument until the mercury appears at the open end. The introduction of liquid is equally easy since, for this purpose, it is only necessary to incline the manometer as before and then, after submerging the open end, to return it to the vertical position.

The enlargement on the manometer does not alone suffice to prevent slipping in the stopper except in the case of quite dilute solutions. If no further precautions are taken, the manometer usually rises until the upper third or half of the enlargement is within the lower end of the stopper, giving rise to a dilution of the solution of unknown and undeterminable magnitude. To prevent this we proceed as follows: Several hours before a manometer is to be used, the stopper, after it has been softened to the right degree (between the teeth, and *not with a caustic alkali*), is cemented with a rubber solution to the tube just above the enlargement. It is then tightly tied near the lower end with a single turn of waxed shoemaker's thread. The lower portions of the rubber are thus crowded downwards and made to expand slightly and cover a small part of the upper portion of the enlargement. If the operation has been rightly performed, the enlargement does not

afterwards ascend any farther into the stopper, however great the pressure in the cell.

After closing the cell, the portion of the stopper which remains outside, *i. e.*, above the glass tube, must be made as rigid as possible. Formerly, we sought to do this by tightly winding the upper end of the stopper with strips of insulating tape; but the support thus given to the sides was not always sufficient, and the tape winding has accordingly been discarded for one of waxed shoemaker's thread, which is much more effective.

Another modification of former practice which may properly be mentioned in this connection, concerns the glass tubes which are inserted in the cells for the reception of the manometers. We have had no trouble with the bursting of the clay cells made by ourselves in the laboratory, not one of them having yet cracked under pressure. The glass tubes, on the other hand, have very frequently cracked, not only while under pressure, but perhaps quite as often, and without any apparent cause, while the cells were not in use. When repeatedly subjected to pressure, the glass which we have hitherto employed becomes quite unreliable. To what extent its unfortunate conduct is due to original defects, we are, of course, unable to determine. Great care has always been exercised in the selection of the tubes, and each one has been subjected to all practicable tests before using it; we are, nevertheless, prepared for the breaking of any one of them while closing the cell, or while under pressure, or even while the cell is lying idle. Both the Bohemian and the Jena tubing have been tried with unsatisfactory results, and finally we have resorted to a lead glass which, it is hoped, will prove more durable.

The method of calibrating the manometer has already been fully described,¹ and we have found no reason for making any essential change in that procedure. But certain corrections, which were neglected in the earlier work, are now applied to the measurements of the volume of the air, and these will be mentioned.

When a manometer has been filled and the volume of the

¹ THIS JOURNAL, 34, 6.

enclosed air is determined for the first time, both ends of the mercury column are located in tubes of equal caliber; but when a measurement is made, the case is different. One end of the column is then in the narrow tube, and the other in the much more capacious bulb on the descending limb of the manometer. Accordingly, a correction for capillary depression is in order, and this is now applied to all readings. The magnitude of the correction is determined experimentally for each instrument, and not calculated from the known caliber of the manometer.

A further correction, which is of some importance in the case of concentrated solutions, is for *meniscus*. Under present conditions the air in the manometer is imprisoned between two mercury columns, and the error resulting from the double meniscus is appreciable when the volume of the air to be measured is small. The diameter of the bore of each manometer is, therefore, determined with a view to eliminating this source of error. The form of the meniscus is assumed, according to the custom in such cases, to be strictly spherical.

Possible corrections, which we have not yet applied, are for the deviations in the conduct of air, under pressure, from the laws of Boyle and of Gay-Lussac. But since the deviations are in each case small, even under our highest pressures, and since the errors resulting from them are of a mutually compensating character, they may with propriety be neglected until some other sources of error, of greater effect upon the results, have been brought under better control. The same may be said of a correction for the distension of the cell under the pressure of its contents. The cell is undoubtedly somewhat expanded during the measurement of pressure, and the solution is therefore somewhat more dilute than it is assumed to be. But dilution due to a distension of the cell under pressure is probably small as compared with that from another cause, which will be mentioned. When a cell is filled with a solution for a measurement of pressure, the porous wall is full of water and some time elapses before the cell can be effectively closed. In the meantime the solution within is rapidly diluting itself by sucking in water from without. We have not

yet been able to devise any means of preventing this dilution of the solution, and must still content ourselves with an endeavor to keep it within bounds by manipulating with the greatest rapidity which is consistent with the safety of the cell and the manometer.

An improvement in our cathetometer, which we devised for the purpose of facilitating final adjustments of the telescope and for determining the distance of any point on the scale from the line above or below it, *i. e.*, for reading the fractions of a millimeter, will perhaps have an interest for others. The usual arrangement for final adjustment on cathetometers of the type of ours tilts the telescope to one side. The design of the elevating device in these instruments is such that the pressure is applied only on one side of the sliding collar upon which the telescope is mounted, whereas it should be applied on all sides equally. If, therefore, the collar is in the smallest degree imperfectly fitted to the rod along which it glides, side-wise displacements are bound to occur. The simple device shown in Fig. VIII. not only remedies this difficulty, but it provides at the same time a satisfactory substitute for the micrometer eye-piece of the telescope.

The upper and heavier end of the set collar *a* has cut upon it a thread of 1 mm. pitch, over which runs the internally threaded, milled and graduated collar *b*. The whole weight of the telescope and its balanced carriage rests upon *b* at *c*, and is uniformly distributed. Upon *e*, but not seen in the figure, is a zero line and, on either side of this, a vernier scale. The raising and lowering of the telescope in the final adjustment is effected by turning *b* to the right or left, and without any tilting or sidewise displacement of the instrument. Considered as a substitute for the micrometer eye-piece, the arrangement has several advantages. In the first place there is no "backlash" in the threaded parts because the pressure is always upon the same side of the thread, whether the telescope is moving upwards or downwards. Secondly, it is not necessary to have the standard scale located at some fixed distance from the telescope. In other words, the correctness of the readings is not dependent on the distance of the object, hence the de-

vice may be used for measurements upon objects at different distances, *e. g.*, upon the standard scale, and a manometer which is nearer or more distant than the scale. Finally, it is more correct in principle than the micrometer eye-piece, since all the various lines of vision are parallel to each other.

Some change has been made in the process for the removal of air from the porous walls of the cells previous to the deposition of the membranes. It is still removed by means of electrical endosmose, but the texture of the cells is so dense that water passes through the walls very slowly—probably not one-tenth as fast as through the walls of the best cells which were made for us by the potters. This great density of texture was found to be an indispensable characteristic of good cells, and without it we have never been able to obtain maximum pressures. But with increasing closeness of texture in the cell wall came diminishing endosmose, and we were, therefore, impelled to search for an electrolyte which should give a more rapid endosmose than the potassium sulphate which we had previously employed. Accordingly, a series of quantitative comparisons was made by one of us (Frazer) of salts having a common anion, with a view to ascertaining which of the cations would, under our conditions, carry the water through the cell wall most rapidly. Lithium was found to be far more efficient in this respect than potassium or any other metal of the alkalis or alkaline earths. Hence we now employ lithium sulphate for the expulsion of air.

The results of the work mentioned above appear to suggest the existence of a definite relation between the velocity of migration of ions and endosmose. The slower the cation the larger the endosmose has been found to be, and the general rule which is deducible from the measurements at hand is the following: *The quantities of water carried through the porous wall, under identical conditions, are inversely proportional to the relative velocities of the various cations divided by their respective valencies.* All of the results conform, within 3 per cent, to this rule, and the subject has been thought worthy of the more extensive and careful investigation which is now in progress in this laboratory.

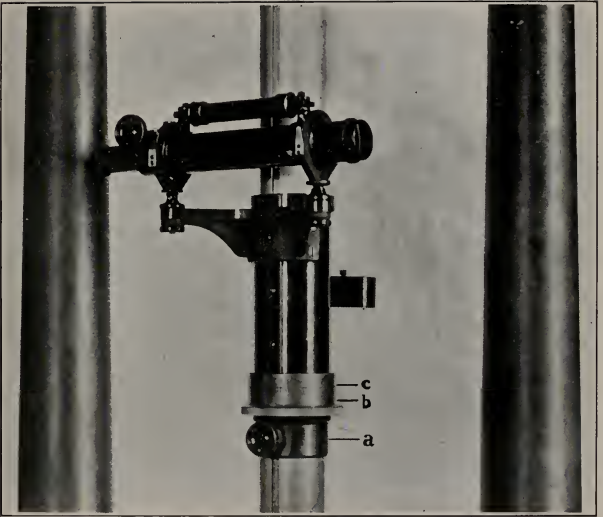


Fig. VIII.

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Some of the observations which we have made regarding membranes may be of assistance to others who are working in the same line, and we shall venture to formulate briefly those which have been frequently verified and have proved useful to us, though in doing so we shall run the risk of repeating some facts which have been stated elsewhere.

1. The resistance of a membrane appears to depend principally upon the porosity of the cell in which it is deposited. The finer the pores of the cell the higher will be the maximum resistance of the membrane. It follows that each cell should be found to have a maximum membrane resistance which is characteristic of itself, and this is true, within certain limits, of all the cells with which we have worked. The cells differ greatly among themselves in this respect. For example, the maximum obtainable resistance in one may be between 30,000 and 40,000 ohms, in another between 90,000 and 100,000 ohms, and in a third perhaps over 300,000 ohms. If the membrane in a given case fails to reach approximately the maximum resistance which is characteristic of its cell, it is known that some trouble exists, and that no reliable measurements will be obtained by setting the cell up with a solution. The nature of the trouble is always obscure, but the remedy which is usually effective consists in soaking the cell for several hours in distilled water. On repeating the membrane-forming process, a higher resistance is invariably obtained, but it may be necessary to repeat the soaking several times before the maximum is reached.

2. The pressure rises more rapidly at first in a cell whose membrane resistance is low, *i. e.*, in a quite porous cell than in one in which the membrane has a high resistance, but the maximum pressure of a solution is developed in a shorter time in the latter than in the former. In general, it may be said that the higher the resistance of the membrane, the shorter will be the time required for the development of maximum pressure. For example, a solution may develop its highest pressure within 3 hours in a cell with a resistance of 300,000 ohms, but not within 24 hours in one in which the resistance is 100,000 ohms.

3. The concentration of a solution appears to have no relation whatever to the time required for the development of maximum pressure. With a given cell a normal and a one-tenth normal solution of the same substance require nearly the same time, provided the resistances of the membranes are about equal in the two cases.

4. Solutions of different substances reach their highest pressures in different times. A solution of glucose, for instance, is much slower in reaching its maximum pressure than is one of cane sugar. It appears probable, though we cannot yet affirm it positively, that, in general, substances of large molecular weight develop their highest pressures more quickly than those of small molecular weight.

5. The first membrane which is deposited in a cell will rarely give with any solution the highest pressure which is known to be normal to it, and it may give only a small fraction of it. Hence it is necessary in all cases to build up a membrane by degrees. The procedure which we have found best adapted to this purpose is the following: The new cell is subjected to the membrane-forming process until the resistance becomes stationary and has continued so for some time, or until it exhibits a tendency to decline. The cell is then soaked for several hours in water, and the first treatment is repeated. The membrane may, on the second trial, exhibit the same maximum as before, but it is probable, if the construction of the cell is mechanically perfect, that the resistance will go higher. But, whatever the result on the second trial, the procedure is repeated in all its details again and again until it is certain that the resistance can be forced no higher by further repetitions, and until it is thought that a sufficient body of the membrane has been deposited. Since the current is exceedingly small, a very long time is required for the precipitation of enough of the copper ferrocyanide to cover adequately the whole interior of the cell, and one is liable to a miscalculation as to the readiness of the cell for the next stage of its development.

The highest *habitual* resistance which is developed by the first course of treatment may not be, and usually is not, the

same as that which afterwards comes to be recognized as the characteristic maximum resistance of the cell. A *packing* and *mending* process is still necessary in order to prepare the membrane for use, and until this is completed one cannot hope to obtain reliable measurements of pressure. It appears that, notwithstanding the high resistance of the membrane at the close of the first stage of its development, it is still not so tightly pressed against the cell wall that it cannot be ruptured by pressure. The second process is, therefore, one of rupturing the membrane, wherever possible, by pressure, of crowding it more tightly against the cell wall by the same means, and of mending simultaneously the rents which have been produced. The cell is set up with a fairly concentrated solution of cane sugar—usually 0.5 weight normal—to which has been added a certain amount of potassium ferrocyanide; and to the water in which the cell is immersed there is added an equivalent amount of copper sulphate. One might expect, in view of the fact that the material which is employed in mending the rents is deposited under pressure and, therefore, close to the wall, that the solution would in time develop its normal maximum pressure, but it rarely does so. The pressure rises, often with considerable rapidity, to a maximum which may be maintained for a long time, but this highest pressure is usually considerably below what the normal maximum for the solution is known to be. When it is found that no higher pressure is developed by longer standing, the cell is taken down, emptied, rinsed, soaked in water which is frequently renewed, and then it is again subjected to the membrane-forming process. A higher resistance than the previous maximum will probably be obtained. If so, the cell is again set up with a solution of cane sugar containing potassium ferrocyanide, etc. If, on the other hand, the membrane exhibits a lower, or no higher, resistance than it did before the cell was set up with the sugar solution, the cell is repeatedly soaked in water and resubjected to the membrane-forming process until no further improvement in the resistance of the membrane can be effected, when it is again set up with a solution of sugar. This process of bursting the membrane and of mending the rents, alternately under pres-

sure and by means of the current, is continued until it reaches an habitual maximum of resistance beyond which it cannot be forced, and until the cell gives, within a reasonable time, what are known to be normal maximum pressures with solutions of cane sugar.

We have described our method of preparing a cell in considerable detail because we know from long experience and from many failures that no reliable measurements of osmotic pressure can be obtained with a membrane which has been prepared with less care, or which has been less-thoroughly tested. The pains we take with our membranes is certainly the minimum which will give any validity to the results, and, in our judgment, speculation based upon measurements with membranes which have been less carefully tested as to their efficiency is utterly futile.

6. It may properly be asked what assurance we have that the highest pressures which we obtain are really the *true* maximum pressures of the solutions; whether, in other words, it is not possible that, with still better membranes, even higher pressures would be obtained. We have had this question constantly before us, and have tried to answer it in the only possible way, that is, by trying continually, in every way known to us, to improve the membranes. The result is that we obtain always the *same* maximum of pressure for a given concentration of cane sugar solution, despite our efforts to produce a membrane which will give a still higher pressure.

The question of *leakage* by the membrane is involved with that of maximum pressures, and it has not been neglected. It has, in fact, been tested in every practicable way—by careful examination of the liquid in which the cell was immersed during the development of pressure, and by determination of the concentration of the cell contents afterwards, and our experience in this direction may be summed up as follows: Membranes may be prepared, in the manner described above, which are wholly impermeable to cane sugar up to weight-normal concentration of solution. If prepared with less care, they usually leak, and the failure of many membranes to give the highest pressures is due to leakage. A solution in a cell with

a leaking membrane may exhibit a nearly constant pressure for a long time, thus giving one who has had but little experience with membranes the impression that he is observing the true maximum pressure of the solution. The difficulty of preparing non-permeable membranes increases as the molecular weights of the substances diminish. A membrane which is non-permeable to cane sugar may, for instance, leak glucose. It is still possible to obtain satisfactory measurements of osmotic pressure by a differential method, even though the membrane is not wholly non-permeable to the substance in solution. If the leakage is slight, we find that the pressures rise to a highest value and remain constant for a considerable time; and that the same result is reached, time after time, with a given concentration of solution, showing that in such cases an equilibrium of conditions is established, under which, it is to be supposed, the solution is exerting its maximum pressure. If so, and the concentrations of the solutions both within and without the cell can be determined, we may obtain all the data which are necessary for a correct interpretation.

The leakage of membranes can be considerably diminished, and in some instances entirely stopped, through the coöperation of the membrane-forming salts. It was stated¹ in the account given of the first series of measurements of the osmotic pressure of cane sugar solutions that we always added to the solution a small amount of potassium ferrocyanide, and to the water on the outside of the cell, a small equivalent quantity of copper sulphate. This practice has been continued. The quantities of the salts so used (and which are still used) were, per 100 grams of water, 8.46 milligrams of the ferrocyanide and 12.48 milligrams of copper sulphate. It was assumed that these quantities of the salts are osmotically equivalent and that, being on opposite sides of the membrane, the pressures of the solutions in the cells would not be affected by their presence. The assumption was, however, based on the supposition that potassium ferrocyanide dissociates in dilute solutions into *five* ions, whereas the recent work of Jones and Bassett² on the depression of the freezing points of solutions of this salt make it

¹ THIS JOURNAL, 34, 31.

² *Ibid.*, 34, 311.

appear probable that the dissociation is into *eight* ions instead of *five*, as formerly supposed. If this is true, there may have been a slight excess of pressure in our cells, due to a lack of osmotic equality between the quantities of ferrocyanide and sulphate which were used, and it may, therefore, be necessary to apply a small correction when the exact magnitude of the discrepancy has been ascertained.

The use of the membrane-forming salts in the manner indicated is of great service in the measurement of pressure, and it appears probable that the efficiency of few membranes could be long maintained without their coöperation. It appears probable, moreover, that it will be desirable, and perhaps necessary in some instances, to employ them in larger quantities than hitherto in cases where it is otherwise difficult or impossible to prepare a membrane sufficiently non-permeable to the substance in solution. Accordingly, we have undertaken to ascertain for ourselves the state of dissociation and the actual osmotic inequalities of the two salts, not only in the quantities we desire to use, but also, as nearly as possible, under the same experimental conditions. The results already obtained indicate that a very small correction is to be applied for an overpressure on the part of the ferrocyanide when the quantities and the relative proportions of the membrane-forming salts are such as we have hitherto employed.

Soon after beginning the measurement of the osmotic pressure of glucose solutions, there appeared upon one of our cells an abundant growth of a fungus, which, upon examination, was found to be *penicillium*. Within a few days it appeared upon one after another of the remaining cells until all were affected in the same manner as the first. We then exposed several solutions of glucose to the air of the laboratory, and the fungus appeared in all of them in a short time. We had had no similar experience previously, though we had worked with solutions containing invert sugar for more than two years, and the conditions under which we were working were, in general, unfavorable to the fungus. The sudden prevalence of *penicillium* spores in the atmosphere of the laboratory could, however, be accounted for, though it had not been anticipated.

At the time, certain changes were in progress in a lower part of the building which involved the tearing away of old walls, and the atmosphere of all parts of the laboratory was, in consequence, in a somewhat dusty condition.

It could not be doubted that the same growth extended over the interior walls of the cells, and that its development there would be attended by chemical changes in the glucose whose effect upon the pressures of the solutions could not be ascertained or estimated. The situation was rendered still more difficult to deal with by certain facts which have been frequently verified and have often given us trouble. All of our experience has been to the effect that anything which acts chemically upon the membrane, even in a slight degree, or which tends to modify its physical condition, destroys its efficiency; and that when a membrane has once been injured in either of these ways, it is difficult, and in the majority of cases impossible, to restore it to a sound condition.

It was clear then that some poison for the *penicillium* must be found which would fulfil the following conditions: (1) It must be effective in such small quantities that the pressure of the solutions would not be sensibly effected by its presence; (2) it must not act chemically or otherwise upon the membrane; and (3) it must have no chemical action upon the glucose. It was desirable, moreover, that the substance should be one which would, at the same time, prevent ordinary alcoholic fermentation, though it had been found that this could be avoided by other suitable means.

We were, therefore, greatly restricted in the choice of agents for the destruction of *penicillium* with which the cells had become infected, and for the prevention of its development in the solutions of glucose. Everything of an alkaline or of a distinctly acid character was excluded from the outset, and the information which was accessible to us regarding the action of other possible agents was exceedingly meager and indefinite. Poisons of the phenol type appeared most likely to serve the purpose, but no specific information could be obtained as to their efficacy in the case of *penicillium*. Therefore a series of simple experiments was undertaken with phenol, salicylic

acid and thymol, and to this list of substances were added hydrocyanic acid and chloroform. Some experiments were also made with potassium cyanide, though no assistance could be expected from this compound, because of its alkaline character and its action upon other cyanides.

All the test solutions were made 0.5 weight normal with respect to glucose, and they were freely exposed to the air while under observation. During the daytime they were maintained at a temperature of 30°, and at night they were placed where the temperature did not fall much below 20°.

1. *Salicylic Acid*.—Two solutions of glucose, one of which contained salicylic acid in the proportion of 5.5 grams per 1,000 liters, were exposed. The presence of *penicillium* became apparent in the pure sugar solution on the fourth day, and in the solution containing the salicylic acid, on the seventh day.

The experiment was repeated with double the amount of salicylic acid—i. e., 11 grams per 1,000 liters—in one of the solutions. The fungus appeared in the solution containing only glucose on the third day, and in that containing salicylic acid on the sixth day.

It was clear that salicylic acid, in the concentration employed, could at best only retard the development of *penicillium*. Nevertheless, it was decided to ascertain whether the acid is injurious to the membrane. Accordingly, a cell, which had previously conducted itself in a satisfactory manner, was set up with a 0.5 N solution of glucose containing 11 grams of salicylic acid per 1,000 liters. It failed to develop the full normal pressure, and on the third day the mercury in the manometer began to fall. It was therefore concluded that the salicylic acid had probably attacked the membrane.

2. *Phenol*.—A 0.5 N solution of glucose was made 0.001 N with respect to phenol. The *penicillium* appeared on the seventh day and grew rapidly thereafter. Other similar experiments were tried with similar results, and it was concluded that phenol in very dilute solutions is but little, if any, more poisonous to *penicillium* than is salicylic acid.

3. *Thymol*.—The usual solution of glucose was made 0.001 N with respect to thymol. It remained perfectly clear for 11 days. On the twelfth day it became slightly cloudy. But as the solution had in the meantime nearly lost the characteristic odor of thymol, the experiment was inconclusive. A vigorous growth of the fungus which had developed in a glucose-phenol solution was therefore removed to a fresh one of glucose and thymol. It soon began to diminish in size and continued to shrink until the eighth day, when it was examined under the microscope and found to be apparently dead. But that it was still living was shown by its subsequent revival, after 2 days, in a sterilized Pasteur's solution. Further experiments with thymol showed conclusively that minute quantities of it suffice not only to prevent the development of *penicillium* in glucose solutions, but also, in time, to kill the living fungus, and it remained for us to ascertain whether its presence is without injurious effect upon the membrane. The first experiments along this line were indecisive. An infected cell was soaked for 4 days in a 0.001 N solution of thymol and then subjected to the membrane-forming process. The resistance of the membrane rose quickly to 33,000 ohms, which was its usual and normal value in the cell in question. Such behavior is ordinarily regarded as evidence of the sound condition of a membrane, but on setting the cell up with a glucose solution containing the usual proportion of thymol, it failed to develop more than 60 per cent of the normal pressure. The conduct of the cell on the first trial, however, was probably due to injury to the membrane during the growth of the *penicillium*, for later, after numerous repetitions of the process heretofore described for the improvement of membranes, it was finally restored to a condition in which it gave normal pressures with glucose solutions containing the usual amount of thymol.

4. *Hydrocyanic Acid*.—A vessel containing a solution of glucose in which a large quantity of *penicillium* was growing vigorously was placed under a bell jar beside another vessel containing potassium cyanide, and into the latter acid was dropped from a funnel. After several hours the fungus was

examined under the microscope. It appeared to be dead, and it did not revive when placed in Pasteur's solution.

A cell infected with *penicillium*, which, before its infection, had given normal pressures with cane sugar solutions, and whose normal resistance was about 75,000 ohms, was filled with water and suspended under a bell jar in an atmosphere of hydrocyanic acid gas. After 12 hours it was removed, cleansed, and subjected to the membrane-forming process. In 20 minutes the resistance rose to 40,000 ohms, but immediately thereafter it began to decline, and at the end of 80 minutes its resistance was only 22,000 ohms. On repeating the treatment, after a thorough soaking in water, the resistance rose to 40,000 ohms in 15 minutes. It then began to decline, as on the previous occasion. The cell was nevertheless set up with a 0.5 weight-normal solution of glucose, which was 0.001 N with respect to thymol. The pressure rose to 11 atmospheres and continued undiminished for 3 days. The conduct of this cell during the first stage of restoration is described because it is unusual for a cell, behaving as it did, to give a pressure so near to correct maximum. Its subsequent conduct was not remarkable, since it required ten repetitions of the usual treatment to restore the membrane to sound condition.

5. *Potassium Cyanide*.—Notwithstanding the impossibility of employing potassium cyanide for our purpose, owing to its destructive action upon the membranes, it was of some interest to compare its efficacy as a poison with that of hydrocyanic acid and thymol. A 0.5 N solution of glucose was made 0.001 N with potassium cyanide and exposed in the usual way. On the eighth day the *penicillium* appeared. As the cyanide had probably all disappeared within that time, owing to chemical transformations, a fresh glucose-cyanide solution was prepared, and into it was introduced a vigorous mass of the *penicillium*. The growth of the fungus appeared to be checked for a time, but on microscopic examination the second day, it was found to be living, and on the third day it was again growing vigorously.

6. *Chloroform*.—Solutions containing *penicillium* were exposed to vapors of chloroform and also treated with small

quantities of it in liquid form, but no marked poisonous effects could be observed.

Of all the substances tested, thymol appeared to be the one best suited to our purpose. It was found to be sufficiently poisonous to *penicillium* when used in quantities so minute that the pressures of the solutions are not sensibly affected by its presence; and what is of equal importance, its presence in small quantities appeared to have no deleterious effects upon the membranes. It is also satisfactory as a preventive of ordinary alcoholic fermentation, which must be carefully guarded against in working with solutions of glucose.

It is probable that hydrocyanic acid could also be employed for our purposes, but since its use is attended with great inconvenience, and thymol answers all our requirements, we have not thought it necessary to experiment any further along that line.

An account of the formal measurement of the osmotic pressure of glucose solutions will be given in Part II. of this paper.

JOHNS HOPKINS UNIVERSITY,
May 1, 1906.

A REDETERMINATION OF THE OSMOTIC PRESSURE AND OF THE DEPRESSION OF THE FREEZING POINTS OF CANE SUGAR SOLUTIONS.¹

BY H. N. MORSE, J. C. W. FRAZER, E. J. HOFFMAN AND W. L. KENNON.

The conclusion reached by Morse and Frazer² regarding the magnitude of the osmotic pressure of cane sugar solutions was expressed in the following words:

"Cane sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state. In other words, dissolved cane sugar exerts an osmotic pressure throughout the larger volume of the solution equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent."

¹ The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution.

² THIS JOURNAL, 34, 93 (1905).

This conclusion was the obvious deduction from the results which were obtained by the measurement of the osmotic pressure of thirteen concentrations of solution ranging from 0.05 to 1.0 gram-molecular weight of sugar dissolved in 1,000 grams of water. The authors believed, moreover, that, after devoting several years to the problem, they had developed the method of measuring osmotic pressure to a point where reliable results were to be expected, and they were inclined, therefore, to assign to them a high degree of trustworthiness, and to regard them as probably sufficient to establish the conclusion with which all of them harmonized in so striking a manner.

There were, however, certain reasons why a redetermination of the osmotic pressure of cane sugar solutions should be undertaken. In the first place, the directly experimental quantitative evidence regarding osmotic pressure, which was previously on record, is meager and wholly inadequate to establish firmly any view whatsoever regarding its magnitude. Hence any measurement of the force which has the virtue of precision is at the present time useful, and cane sugar lends itself to work of this kind more readily and over a wider range of concentrations than any other available substance. It is obtainable in any quantity desired and in a high state of purity, is sufficiently soluble, and, above all, it is practicable to prepare membranes which are wholly impervious to it.

In the second place, the method as employed in the first series of measurements was still susceptible of considerable improvements, which, if introduced, would materially reduce or wholly remove certain known sources of error. Moreover, a number of small corrections had been neglected in the earlier work, which, under the improved experimental conditions, could be appropriately applied. It was reasonable to expect, therefore, that results approximating more closely to the real osmotic pressures of the solutions could be secured by a second series of measurements than had been obtained by the first.

It was stated in the earlier communication¹ that the measurements of the osmotic pressure of cane sugar solutions would be repeated at an early date, and that the sources of error to

¹ THIS JOURNAL, 34, 92 (1905).

which particular attention would be given were three in number: (1) The "thermometer effects," (2) the uncertainty regarding the capacity of the closed end of the manometer, and (3) the inversion which takes place in the cell.

The measures which were taken to eliminate the thermometer effects, and the uncertainty regarding the capacity of the manometer in the region in question, have been fully described in the preceding paper (p. 2) and it need only be said of them here that they were effective.

Regarding the last of the three principal sources of error, namely, the inversion which takes place in the cell, some statements made in the first communication will be recalled:

1. The attempt was made to determine the extent of the inversion by the method of Fehling.¹

2. The inversion which took place in the cells was always greater than that which occurred in portions of the same solutions which were set aside for comparison at the close of the experiments.² This observation has been confirmed in all of our subsequent work, but the cause of it has not yet been ascertained.

3. The opinion was expressed³ that the inversion in the more concentrated solutions was, in reality, greater than it was apparently found to be by the method which was employed to determine it, and it was stated that, when the work was repeated, the polariscope would be used to measure the inversion which takes place in the cell. The suspicion that the amount of inversion had been underestimated in the earlier work, which was aroused by observations that could not be tested at the time, has since been confirmed.

In conformity with our purpose to describe adequately whatever is new in our procedure, we shall now state the essential facts concerning the preparations which were made for the polariscopic work.

The instrument used is the Schmidt and Haensch half-shadow polariscope, with double wedge compensation and

¹ *THIS JOURNAL*, 34, 31 (1905).

² *Ibid.*, 34, 30 (1905).

³ *Ibid.*, 34, 92 (1905).

triple field of vision. The length of tube which it accommodates is 4 decimeters, and a small incandescent electric lamp is employed for illumination.

As the basis of the system upon which we are working—a gram-molecular weight of substance dissolved in 1,000 grams of water (both corrected for air displacement)—differs widely from that ordinarily employed in saccharimetric work, it was necessary either to recalculate the standard data and find their values in terms of our system, or to construct a table of corrections from data obtained by ourselves. We followed the former course, taking the precaution, however, to verify experimentally several of the computed results. It is not necessary to explain the method of calculation, but we give in full the table of corrections which was computed and has been used in the present work. The values appearing in the table are the weights of invert sugar which, in a 2 decimeter tube, produce a loss of 1° in rotation (at 19° , 20° , 21° , 22° and 23°) in the solutions whose pressures we have measured.

Table I.—*Invert Sugar in Grams per 1,000 Grams of Water, which Produced a Loss of 1° in Rotation.*

Weight-normal concentration.	Temperature.					
	18° .	19° .	20° .	21° .	22° .	23° .
0.10	2.12	2.13	2.14	2.15	2.15	2.16
0.20	2.16	2.17	2.18	2.19	2.20	2.21
0.30	2.21	2.22	2.23	2.23	2.24	2.25
0.40	2.25	2.26	2.27	2.28	2.29	2.30
0.50	2.31	2.32	2.32	2.33	2.34	2.35
0.60	2.34	2.35	2.36	2.37	2.38	2.38
0.70	2.38	2.39	2.40	2.41	2.42	2.43
0.80	2.43	2.44	2.44	2.45	2.46	2.47
0.90	2.47	2.48	2.49	2.50	2.51	2.52
1.00	2.51	2.52	2.53	2.54	2.55	2.56

Since one molecule of cane sugar yields two of invert sugar, the correction for inversion is made by deducting from the observed pressure one-half the calculated pressure of the invert sugar which is found by the polariscope. The loss in rotation may, however, not be due exclusively to inversion. A part of it may result from a *dilution* of the cell contents, and dilution may, in turn, be brought about by an increase in the capacity

of the cell, or by a leaking of the membrane. The last source of error, leakage, is excluded by the pains we have taken in the present work to ascertain that the membranes employed were really impervious to cane sugar. On the other hand, some loss of rotation from dilution, due to an increase in the capacity of the cell, has at times been unavoidable, and it will be seen later on that we have, in a few cases, attempted to discriminate between inversion and dilution as causes of the diminished rotation of the solutions.

All that need be said regarding the preparation and the testing of the membranes has been fully explained in the preceding paper. It may not be superfluous, however, to restate here, in a general way, the more important facts concerning them, namely: (1) That the membranes are prepared for their work by an elaborate and time-consuming course of treatment, involving deposition by the current, followed by a bursting of them by pressure and a mending of the rents, first under pressure and subsequently by the current, until a resistance is reached which can be forced no higher by a continuation of the process; (2) that the membranes are tested as to their permeability by examining the water in which the cells are immersed during an experiment for the presence of the dissolved substance. The results given in this paper were all obtained with membranes which did not leak cane sugar.

The method of calibrating the manometers, which was explained in a former paper,¹ has been adhered to without any essential modification. On the other hand, important changes have been made in the form of the manometer and in the method of closing it and preparing it for insertion in the cell. All of these matters have been discussed in the preceding paper (p. 20), and certain of them will be mentioned again in connection with an account of the corrections which have been applied to the measurements of pressure.

The values given in the present paper are all computed on the basis of *one* for the atomic weight of hydrogen. The theoretical molecular weight of cane sugar is, therefore, 339.6 instead of 342.22, which was the value used in the earlier

¹ THIS JOURNAL, 34, 6 (1905).

paper. Accordingly, the standard weight of the theoretical gas becomes 2 grams instead of 2.02 grams, and its theoretical pressure, under standard conditions of volume (1 liter) and of temperature (0°), at Baltimore is 22.265 atmospheres instead of 22.488 atmospheres. On this basis, the formula for computing molecular weight¹ from osmotic pressure is

$$M = W \frac{22.265 + 0.0817t}{P},$$

in which M is the molecular weight, P the observed osmotic pressure, W the weight of the substance dissolved in 1,000 grams of water, 22.265 the theoretical pressure of a gram-molecular weight of a gas at 0° when its volume is reduced to 1 liter, and 0.0817 is the temperature coefficient, either of gas or of osmotic pressure.

It will hardly be necessary to recall the fact that our solutions are all made by dissolving a gram-molecular weight of the substance, or some decimal part thereof, in 1,000 grams of water, and that both weights are corrected for air displacement. The material used in the present investigation, as in the earlier one, was the purest obtainable "rock candy."

The corrections which have been applied are numerous, and some of them are of considerable importance. All of them have, however, been discussed more or less fully elsewhere, particularly in the preceding paper, and a brief recapitulation will suffice for present purposes, except in the case of the correction for inversion.

1. *The Correction of the Manometer for Inequalities of Bore.*—The method of calibrating a manometer is explained in the first paper² on the measurement of the osmotic pressure of cane sugar solutions, and, as stated above, we have found no reason for changing in any essential respect the procedure there described. The manometers used in the present work were calibrated with unusual care, and in each case with repetitions of the procedure until all the discordances in the recorded data were well within the limits of reasonable errors of observation.

¹ THIS JOURNAL, 34, 32 (1905).

² *Ibid.*, 34, 6 (1905).

The uncertainty regarding the true volume of the manometer in the region of the closed end was pointed out¹ in the same paper, and the means by which this difficulty and another of analogous character were finally overcome are explained on page 21 of the preceding communication.

In this connection may also be mentioned, as having an indirect bearing on the accuracy of the results, the later improvements² in manometers, consisting in the introduction of a bulb on the ascending limbs and the substitution, for the bulb near the open ends, of a thick spherical mass of glass which is made without increasing the bore of the tube.

2. *The Correction for Capillary Depression.*—As explained on page 26, when the volume of the air in a manometer is determined for the first time, no correction for capillary depression is necessary because both ends of the mercury column which separates the gas in the manometer from the outside air are located in tubes of the same internal diameter. The case is different when a measurement is made. The increasing pressure in the cell drives the mercury column forward until its rear end is within the bulb on the descending limb of the manometer, the diameter of which is many times that of the other end of the column, and a correction for capillary depression is therefore necessary. We have determined experimentally the magnitude of this correction for each of the manometers which was used in the present work, and it has been applied to all the measurements here recorded.

We have been duly mindful throughout of the fact that, in manometric work in narrow tubes, gross errors may result from an impure condition of the mercury, and great care has been taken to prepare the mercury which is used in the manometers in the highest possible state of purity.

3. *The Correction for Meniscus.*—In the form of manometer now used by us, the air is located between two mercury columns, and the correction for meniscus is of considerable importance when the pressure of a concentrated solution is measured. The following example will illustrate this: Under a pressure of 25 atmospheres, approximately that of a weight-

¹ THIS JOURNAL, 34, 10 (1905).

² *Ibid.*, 36, 22 (1906).

normal solution at 25° (not corrected for atmospheric pressure) the length of the air column is reduced to about 18 mm. in one of the manometers, and the correction for the double meniscus is about 0.2 mm., or nearly 0.3 atmosphere. In order to ascertain the magnitude of the correction to be applied for meniscus, the internal diameter of each manometer is determined by the usual micrometric method, and the volume of the meniscus is calculated on the assumption that the end of the mercury column is hemispherical in form when its diameter does not much exceed 0.5 mm.

4. *The Correction for Liquids in the Manometer.*—When a cell is closed and the manometer nut is screwed down upon the stopper for the purpose of fixing the latter firmly in its place and of bringing a suitable initial pressure upon the contents of the cell, the solution enters the manometer, pushing the mercury before it until the surface of contact between the two has receded to some point in the bulb on the descending limb of the manometer. We have thus two liquids in the manometer whose pressure must be ascertained and added as a correction to that which is calculated from the volume of the air, and the magnitude of this correction must be determined in part before the cell is placed in the bath, because afterwards nothing is in sight except that portion of the manometer which contains the air. The virtual height of the solution is the difference in level between the water outside of the cell and the surface of contact between the two liquids in the manometer bulb, and this is determined at once by the cathetometer. The density of the solution is, of course, known. The virtual height of the mercury is the difference in level between the surface of contact in the bulb and the upper end of the column, the position of which is not fixed until the pressure becomes constant. It is, therefore, necessary in this preliminary work to determine the difference in level between the surface of contact of the two liquids in the bulb and some fixed point on the ascending limb of the manometer, which is always in sight. The difference in level between the point of reference and the top of the mercury column can then be ascertained at any time, and the correction for the adverse pressure of mercury com-

pleted. The necessary fixed points of reference are provided for by etching upon the manometer tubes two fine lines, one of which is located near the bottom and the other near the top of the ascending limbs. The assumption is made that when the cell is ready to be placed in the bath no further movement of the surface of contact between the two liquids in the bulb occurs, which is not strictly true. But, inasmuch as the manometer nut is screwed down in all cases until a relatively high initial pressure has been obtained, and the diameter of the bulb is many times that of other parts of the manometer tube, the error resulting from this unavoidable assumption is insignificant.

The presence of a small portion of the solution in the bulb of the manometer, at a considerable distance from the membrane through which water enters the cell, and in the narrow channel connecting this portion with the main body of the solution, could not fail to bring to the front at once a question of importance, namely, the question (to state it in a general way) of the *distribution of the water which passes through the membrane into the solution.*

We can only say that we attacked the problem experimentally more than three years ago and found it an excessively difficult one to solve and that we have not yet enough well established facts to justify any discussion of the subject on our part. Nevertheless, a brief statement of our procedure may not be out of place. We attempted to determine at intervals the concentration of the solution at different distances from the membrane, but were thrown into confusion by the discovery of the fact that water passes through the membrane at different rates in different areas, and that the rate of passage in the different areas depends on the porosity of the wall behind them. As we could produce no cells with perfectly uniform porosity throughout, this line of investigation was abandoned, and we afterwards devoted six months to experimenting upon the effect of stirring the solution on the rate of intake of water, and on the final magnitude of the pressures. Here, again, we were baffled by the complexity of the determining conditions, and the data which we gathered have no present value, though it

is hoped that later they may contribute something toward the solution of the problem. We do not hesitate to express the opinion that any theoretical solution of it will be unsatisfactory, owing to the impossibility of giving due weight to each one of the many conditions which are involved. We have not, up to this time, made any observation which has led us to suspect that we are getting less than maximum pressures because of a failure on the part of the water taken into the cell to distribute itself with sufficient rapidity or sufficiently uniformly through the solution.

5. *The Correction for Loss in Rotation.*—We have stated already that the diminished rotation of the solutions is due to two causes: First, and principally, to the inversion of the cane sugar which occurs in the cell, and secondly, to an increase in the capacity of the cell which is necessarily followed by dilution. Dilution from leakage, as we have already explained, is excluded by the care we have taken to ascertain that no sugar had escaped from the cell. It is not possible in any case to determine exactly how much of the loss in rotation is due, on the one hand, to inversion, and, on the other, to dilution; but it is safe to affirm that, in our experiments, the loss from the second cause is usually so small as compared with that from the first, no great error is committed by ascribing all loss of rotation to inversion. In a few instances, nevertheless, we have attempted, as will be seen later, to assign a certain minimum value to the dilution effect.

Dilution of the cell contents, excluding that due to a possible escape of the dissolved substance, is brought about in various ways, which will be enumerated:

(a) The capacity of the cell is, doubtless, somewhat increased in consequence of a distension of the containing walls under pressure. We have taken no measure up to the present time to ascertain the magnitude of this effect, but it is believed to be small and safely negligible until other sources of error have been brought under better control. We have taken the trouble, however, to assure ourselves occasionally that the length of the manometers is not sensibly increased by the highest possible pressures. The test is easily made by measuring

the distance between the two reference lines on the vertical limbs.

(b) When the cell is filled and closed, a certain "initial" pressure is brought upon the contents by mechanical means, but, as this is always less than the final osmotic pressure of the solution, there is a subsequent rise of the mercury in the manometer, and the space occupied by the solution is increased by an amount exactly equal to the contraction of air in the manometer. The volume of the water which is thus taken into the cell to expand the solution to its new and final limits is known, for we determine not only the inequalities of bore in the manometers, but also the absolute volume of the calibration units. We are, therefore, prepared to calculate at any time the extent of the dilution of the solution from the cause under consideration. If we take into account (1) the fact that the "initial" pressures are the highest which we consider it safe to establish, (2) that the internal diameter of the manometer tubes is very small—ranging between 0.5 and 0.6 mm., and (3) that the capacity of the cell proper is between 18 and 25 cc., it will be seen that the volume of the water taken in is insignificant as compared with the original volume of the solution, and that its effect as a diluent may be neglected.

The knowledge of the absolute volumes of the calibration units is useful in another way. It enables us to ascertain at any time the exact volume of the solution which is within the manometer, and therefore to form a rough estimate of the effect upon pressure if this less fortunately situated portion of the solution should fail to obtain its due share of the water which enters the cell through the membrane.

(c) As mentioned elsewhere, when a cell is filled with a solution some time elapses before it can be closed and the proper amount of "initial" pressure can be brought to bear upon the solution. In the meantime the solution is sucking in water from the wet porous wall, and constantly becoming more dilute. There are no means of wholly preventing this dilution, or of estimating its magnitude. We attempt to keep it down to the lowest limits by inserting the wet cell in a flexible rubber cap, by rinsing the interior of the cell many times

with the solution before filling it, and, finally, by manipulating with the utmost rapidity while closing the cell.

(*d*) We come now to what, in our judgment, is the largest single source of experimental error in our work, namely, the use of the rubber stopper in closing the cell. We have considered or tried every expedient which suggested itself as giving any promise of enabling us to dispense with it, but have found them all less satisfactory, on the whole, than the stopper itself. The difficulty is due, of course, to the lack of rigidity in the stopper. The means which have been resorted to with a view to keeping the stopper in its place, and to rendering the portion of it which remains outside of the cell so rigid that no internal pressure will suffice to increase the capacity of the cell, by crowding upwards either the manometer itself, or portions of the stopper, or both, have been described in various places in these papers. It must be admitted, however, that these measures have not always been effective, and that some dilution of the cell contents, which is due to the cause in question, usually occurs. In the majority of the measurements the effect is so small that no considerable error is committed by ascribing all loss of rotation to inversion. In the remaining cases, as will be explained, the loss in rotation can be approximately distributed between inversion and dilution.

After placing a cell in the bath, the first thing which is determined is the location of the upper reference line on the manometer. The position of this line should remain stationary throughout the experiment, and it will do so if there is no slipping of the manometer in the stopper, or crowding of the material of the latter out of place, either or both of which necessarily sends the manometer upwards. The exact amount of the upward displacement of the manometer is measured in every instance, and, if it were due solely to slipping in the stopper, the resulting dilution of the solution could be quite accurately calculated. But, as a rule, there is, under present conditions, little slipping of the manometer in the stopper. Most of the upward movement of the manometer during an experiment is due, unfortunately, to a distortion of the stop-

per, the effect of which upon the volume of the cell contents cannot be accurately estimated.

In the following table is given the upward displacement of manometer in each of the experiments recorded in this paper. There are also given the corresponding losses in rotation of the cell contents :

Table II.—Displacement of Manometer and Loss in Rotation.

Weight-normal concentration of solution.	Number of the experiment.	Upward displacement of the manometer: mm.	Loss in rotation in degrees.	Weight-normal concentration of solution.	Number of the experiment.	Upward displacement of the manometer: mm.	Loss in rotation in degrees.
0.1	1	0.07	0.5	0.6	1	3.78	2.8
	2	0.54	0.5		2	0.83	1.9
0.2	1	2.78	0.7	0.7	3	0.64	1.8
	2	1.44	0.7		1	0.24	2.6
	3	0.19	0.5		2	0.07	2.2
0.3	1	0.12	0.5	0.8	1	0.32	3.2
	2	0.10	0.6		2	1.80	3.9
0.4	1	0.30	0.8	0.9	1	1.21	2.5
	2	1.18	1.3		2	0.87	2.4
0.5	1	0.16	1.4	1.0	1	0.88	2.4
	2	0.32	1.2		2	2.97	4.0

The smallest upward displacement of the manometer was less than 0.1 mm (0.08 mm.), while the greatest was 3.78 mm. It will be noticed, moreover, on comparing the different determinations of a given concentration with respect to displacement of manometer and loss in rotation that where the former is large the latter is likewise considerable. For example, in the case of the 0.6 weight-normal solution, of which three measurements of pressure were made, the displacements of the manometer were 0.64 mm. (Expt. 3), 0.83 mm. (Expt. 2), and 3.78 mm. (Expt. 1), and the corresponding losses in rotation were 1°.8, 1°.9 and 2°.0. It is reasonable to suppose that the amount of inversion was not greater in Experiment 1 of this series than in Experiments 2 and 3, and that the greater loss in rotation in that case was due to a greater dilution of the

cell contents. That more dilution did take place in Experiment 1 than in 2 and 3 is proved by the greater displacement of the manometer. This assumption has been made the basis of an attempt to discriminate, in a few instances, between loss of rotation due to inversion and that due to dilution. It is assumed, for example, in the case of the 0.6 N solution, as stated above, that the inversion in Experiment 1 was probably not greater than in Experiments 2 and 3, and, therefore, in correcting for loss of rotation in Experiment 1, 1°.8 of the loss is ascribed to inversion and 1° to dilution. This procedure only partially corrects for the dilution of the cell contents, since all crowding of the manometer out of its place is attended by an increase in the capacity of the cell. Hence, in Experiments 2 and 3, some of the loss in rotation is undoubtedly due to dilution though it is all ascribed to inversion. In presenting the results in the latter part of this paper, two tables of data are given wherever an attempt has been made to distribute the loss in rotation between inversion and dilution. In one of these is given the result as it would be if all loss is ascribed to inversion, and in the other the result as it is found to be on distributing the loss in accordance with the plan explained above.

The ideal substance for the precise determination of osmotic pressure is one which suffers no chemical change in the cell, which does not escape through the membrane, and whose concentration of solution can be accurately determined, preferably by the polariscope. With such a substance, all loss of concentration in the cell would necessarily be due to dilution, and the extent of this could be correctly determined.

In Table III. the data given in Table II. are repeated, and there are added other columns showing (1) the deviations of the results, in fractions of an atmosphere from theoretical gas pressures if all losses of rotation are ascribed to inversion, (2) the distribution of the diminished rotation of the cell contents between inversion and dilution wherever such an apportionment has been made, and (3) the differences between theoretical gas pressures and the results when the latter are corrected for dilution :

Table III.

Weight-normal concentration of solution.	Number of the ex- periment.	Upward displace- ment of the man- ometer. mm.	Loss in rotation in degrees.	Deviation from gas pressure if all loss in rotation is ascribed to inver- sion. (Atmosphere.)	Loss in rotation due to inversion.	Loss in rotation due to dilution.	Deviation from gas pressure if correc- tion for dilution is made.
0.1	1	0.07	0.5	+0.10	0.5		
	2	0.54	0.5	+0.13	0.5		
0.2	1	2.78	0.7	-0.14	0.5	0.2	-0.07
	2	1.44	0.7	-0.09	0.5	0.2	-0.02
	3	0.19	0.5	0.00	0.5		
0.3	1	0.12	0.5	+0.03	0.5		
	2	0.10	0.6	+0.03	0.6		
0.4	1	0.30	0.8	+0.03	0.8		
	2	1.18	1.3	-0.11	0.8	0.5	+0.06
0.5	1	0.16	1.4	0.00	1.4		
	2	0.32	1.2	+0.12	1.2		
0.6	1	3.78	2.8	-0.18	1.8	1.0	+0.19
	2	0.83	1.9	+0.15	1.9		
	3	0.64	1.8	+0.23	1.8		
0.7	1	0.24	2.6	+0.02	2.6		
	2	0.07	2.2	+0.03	2.2		
0.8	1	0.32	3.2	-0.05	3.2		
	2	1.80	3.9	-0.23	3.2	0.7	+0.03
0.9	1	1.21	2.5	-0.04	2.5		
	2	0.87	2.4	+0.08	2.4		
1.0	1	0.88	2.4	+0.23	2.4		
	2	2.97	4.0		2.4	1.6	-0.23

The results which were obtained by the measurement of the osmotic pressure of ten concentrations of solutions—ranging from 0.1 to 1.0 gram-molecular weight of sugar dissolved in 1,000 grams of water, are given in the following tables. All of the determinations, with the exception of three, were made in a single cell—that which, according to our system of designation, is called G. The last three determinations were made with A and B, the cells with which we began the measurement of the osmotic pressure of cane sugar. The reappearance of A and B on the work, owing to the cracking of the glass tube in

G, is noteworthy as an indication of the durability of good cells. A and B have been in more or less continuous use for over a year, and were withdrawn from service in the measurement of the pressure of glucose solutions for the completion of the present work.

Every cell has what may be called its idiosyncrasies of behavior. G is noteworthy, among other things, for its high resistance, and for the rapidity with which solutions in it reach a maximum pressure.

Tables IV. to XXX., inclusive, contain, in an abridged form, the record of the individual determinations of pressure. The actual readings by the telescope have been omitted owing to the great space which they occupy. Otherwise the record is purposely made so complete that one can not only follow the development of pressure in every case, but also recalculate the results.

In Tables XXXI. and XXXII. much of the data contained in Tables IV. to XXX. has been brought together under the titles "Summary of Conditions" and "Summary of Results," and some comment upon these tabulations is called for.

1. Table XXXI. *Summary of Conditions.* It will be noticed (column 3) that three different cells, G, A and B, were used in the present work. G is a new cell and has not been employed for other measurements of pressure. It is noteworthy for the high resistance of its membrane, which ranges (column 4) between 372,000 and 158,550 ohms, with a usual value of about 270,000 ohms. The former value is the highest which it has been possible to obtain by repetitions of the course of treatment which has been explained elsewhere. The other resistances given in the table were likewise *maxima* in the sense that they could not be forced any higher without interrupting the current, soaking the cell in water, etc. The minimum, 158,550 ohms, is the lowest resistance with which we have thought it safe to set up the cell for a formal measurement.

A and B are old cells which have been in service nearly continuously for over a year. They are, in fact, the first wholly satisfactory cells which were produced in the laboratory, after

Table V.

Original wt. normal concentration of solution, 0.1. Experiment No. 2.
 Rotation of original solution, $12^{\circ}.8$ ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $12^{\circ}.3$ ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Cell used, G.
 Resistance of membrane, 275,000 ohms.
 Initial pressure, 2.20 atmospheres.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 5.00 P. M., April 9, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.			
April 9.												
8.00 P. M.	24° 15	24° 10	144.56									
April 10.												
12.00 A. M.	24° 20	24° 10	142.45	130.88	0.99	0.51	0.07	0.02	2.53	2.42	+0.11	325.40
8.30 "	24° 20	23° 90	141.31	129.92	0.99	0.51	0.07	0.02	2.56	2.42	+0.14	321.58
11.00 "	24° 25	24° 00	141.36	129.91	0.99	0.51	0.07	0.02	2.56	2.43	+0.13	321.63
12.30 P. M.	24° 25	24° 10	141.32	129.84	0.99	0.51	0.07	0.02	2.56	2.43	+0.13	321.63

Upward displacement of manometer = 0.54 mm.

Upward displacement of manometer = 0.54 mm.

Table VI.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
 Rotation of original solution, 25° ($t = 20^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of experiment, $24^{\circ}.3$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, $0^{\circ}.7$. Resistance of membrane, 271,250 ohms.
 Calibration units of air in manometer, 461.34. Initial pressure, 1.98 atmospheres.
 Time of setting up cell, 12.30 P. M., March 3, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.						
March 3.														
5.50 P. M.	20° 00	21° 64	144.08											
11.00 "	20° 20	22° 00	96.69											
March 4.														
12.00 M.	20° 65	21° 84	95.67	88.57	0.99	0.52	0.10	0.02	4.66	4.79	-0.13	349.10		
7.00 P. M.	20° 85	21° 90	95.71	88.59	0.99	0.52	0.10	0.02	4.66	4.79	-0.13	348.53		
11.30 "	20° 95	21° 94	95.83	88.69	1.00	0.52	0.10	0.02	4.64	4.79	-0.15	350.97		
March 5.														
10.20 A. M.	21° 15	21° 00	95.85	88.60	1.00	0.52	0.10	0.02	4.64	4.80	-0.16	351.21		

See Table VII. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 2.78 mm.

Table VII.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
 Rotation of original solution, 25° ($t = 20^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of experiment, $24^{\circ}.3$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, $0^{\circ}.7$. Resistance of membrane, 271,250 ohms.
 Calibration units of air in manometer, 461.34. Initial pressure, 1.98 atmospheres.
 Time of setting up cell, 12.30 P. M., March 3, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.						Mean molecular weight.		
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.		Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.
March 3.													
5.50 P. M.	20° 00	21° 64	144.08										
11.00 "	20° 20	22° 00	96.69										
March 4.													
12.00 M.	20° 65	21° 84	95.67	88.57	0.99	0.52			0.02	4.73	4.79	-0.06	343.93
7.00 P. M.	20° 85	21° 90	95.71	88.59	0.99	0.52			0.02	4.73	4.79	-0.06	344.16
11.30 "	20° 95	21° 94	95.83	88.69	1.00	0.52			0.02	4.71	4.79	-0.08	345.76
March 5.													
10.20 A. M.	21° 15	21° 99	95.85	88.69	1.00	0.52			0.02	4.71	4.80	-0.09	345.99
Due to inversion = -0.07. Due to dilution = +0.04.													
344.96													

Due to inversion = -0.07.
 Due to dilution = +0.04.

See Table VI.

Upward displacement of manometer = 2.78 mm.

Table VIII.

Original wt. normal concentration of solution, 0.2. Experiment No. 2.
 Rotation of original solution, 25° ($t = 20^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $24^{\circ}.3$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, $0^{\circ}.7$. Resistance of membrane, 280,000 ohms.
 Calibration units of air in manometer, 402.13. Initial pressure, 2.30 atmospheres.
 Time of setting up cell, 4.30 P. M., March 6, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
March 6.	9.10 P. M.	20°.90	22°.04	110.41									
March 7.	10.30 A. M.	21°.20	22°.19	83.05	76.79	1.00	0.58	0.10	0.02	4.74	4.80	—0.06	343.86
	2.20 P. M.	21°.30	22°.25	83.14	76.89	1.00	0.58	0.10	0.02	4.73	4.80	—0.07	344.70
	4.40 "	21°.30	21°.64	83.18	77.06	1.00	0.58	0.10	0.02	4.72	4.80	—0.08	345.43
	9.00 "	21°.35	21°.54	83.62	77.49	1.00	0.58	0.10	0.02	4.69	4.80	—0.11	347.70
March 8.	10.15 A. M.	21°.73	22°.74	84.09	77.61	0.99	0.58	0.10	0.02	4.69	4.80	—0.11	348.14

See Table IX. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 1.44 mm.

Table IX.

Original wt. normal concentration of solution, 0.2.	Experiment No. 2.
Rotation of original solution, 25° (<i>t</i> = 20°).	Manometer used, No. 6.
Rotation at conclusion of experiment, 24° .3 (<i>t</i> = 20°).	Capillary depression, 0.02 atmosphere.
	Cell used, G.
Loss in rotation 0° .7.	Resistance of membrane, 280,000 ohms.
Calibration units of air in manometer, 402.13.	Initial pressure, 2.30 atmospheres.
Time of setting up cell, 4.30 P. M., March 6, 1906.	

Due to inversion = -0.07.
Due to dilution = +0.04.

Original wt. normal concentration of solution, 0.2.
 Rotation of original solution, 25° ($t = 20^\circ$).
 Rotation at conclusion of experiment, 24° .3
 ($t = 20^\circ$).
 Loss in rotation 0° .7.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 4.30 P. M., March 6, 1906.

Experiment No. 2.
 Manometer used, No. 6.
 Capillary depression, 0.02 atmosphere.
 Cell used, G.
 Resistance of membrane, 280,000 ohms.
 Initial pressure, 2.30 atmospheres.

See Table VIII.
 Upward displacement of manometer = 1.44 mm.

Table X.

Original wt. normal concentration of solution, 0.2. Experiment No. 3.
 Rotation of original solution, $24^{\circ}.9$ ($t = 20^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $24^{\circ}.4$ Capillary depression, 0.02 atmospheres.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, 0.5. Resistance of membrane, 225,400 ohms.
 Calibration units of air in manometer, 402.13. Initial pressure, 2.13 atmospheres.
 Time of setting up cell, 4.50 P. M., March 8, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquid in manometer.	Inversion.	Capillary depression.						
March 8.														
8.30 P. M.	21° 50	22° 44	86.15		0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.37		339.74
March 9.														
12.45 A. M.	21° 65	22° 64	83.00	76.63	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.54		
8.30 "	21° 80	22° 69	83.02	76.64	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.54		
10.30 "	21° 85	22° 74	83.15	76.74	0.98	0.59	0.07	0.02	4.80	4.81	-0.01	340.31		

Upward displacement of manometer = 0.19 mm.

Table XI.

Original wt. concentration of solution, 0.3.	Experiment No. 1.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
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Original wt. normal concentration of solution, 0.3. Experiment No. 1.
 Rotation of original solution, 36°.5 ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 36° ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 0°.5. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 275,000 ohms.
 Time of setting up cell, 4.00 P. M., March 14, 1906. Initial pressure, 3.50 atmospheres.

Table XII.

Original wt. normal concentration of solution, 0.3. Experiment No. 2.
 Rotation of original solution, $36^{\circ}.6$ ($t = 15^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 36° ($t = 15^{\circ}$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $0^{\circ}.6$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 273,250 ohms.
 Time of setting up cell, 1.00 P. M., March 17, 1906. Initial pressure, 3.40 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer, etc.	Inversion.	Capillary depression.							
March 17.															
5.00 P. M.	19°.65	21°.75	56.88												
9.00 "	19°.70	22°.20	56.75	52.47	1.01	0.62	0.08	0.02	7.21	7.16	+ 0.05	337.36			
March 18.															
12.00 A. M.	19°.85	22°.34	56.80	52.50	1.01	0.62	0.08	0.02	7.21	7.16	+ 0.05	337.53		338.2	
11.15 "	20°.10	21°.34	56.85	52.72	1.02	0.62	0.08	0.02	7.17	7.17	0.00	339.70			

Upward displacement of manometer = 0.10 mm.

Table XIV.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
 Rotation of original solution, 48° ($t = 17^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $46^\circ.7$ ($t = 17^\circ$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $1^\circ.3$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 277,500 ohms.
 Time of setting up cell, 5.15 P. M., March 12, 1906. Initial pressure, 4.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Elect.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	
March 12.													
8.00 P. M.	22° .00	22° .44	47.31										
March 13.													
12.00 A. M.	22° .10	22° .59	43.27	39.96	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.47	
10.00 "	22° .15	22° .44	43.29	40.00	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.52	
12.30 P. M.	22° .20	22° .60	43.29	39.98	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.58	

See Table XV. for distribution of loss in rotation between inversion and dilution.

Upward displacement of manometer = 1.18 mm.

Table XVI.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
 Rotation of original solution, 59° ($t = 20^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., 57.6 ($t = 20^\circ$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $1^\circ.4$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 274,500 ohms.
 Time of setting up cell, 4.30 P. M., March 19, 1906. Initial pressure, 10.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.						Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
	Solution.		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.					Osmotic pressure, corrected.
March 19.															
8.30 P. M.	22°.60	22°.80			34.61										
11.30 "	22°.65	22°.50			34.55	31.92	0.98	0.65	0.22	0.02	12.07	12.06	+0.01	339.26	
March 20.															
8.00 A. M.	22°.50	22°.50			34.55	31.92	0.99	0.65	0.22	0.02	12.06	12.05	+0.01	339.36	339.59
11.30 "	22°.70	22°.60			34.62	31.97	0.99	0.65	0.22	0.02	12.04	12.06	-0.02	340.16	

Upward displacement of manometer = 0.16 mm.

Table XVII.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.		
March 23.													
8.15 P. M.	23°.70	24°.70	39.67										
March 24.													
12.00 A. M.	23°.70	24°.10	39.29	36.10	39.29	36.10	1.02	0.60	0.19	0.02	12.19	12.10	337.11
9.15 "	23°.70	23°.70	39.10	35.97	39.10	35.97	1.02	0.60	0.19	0.02	12.25	12.10	335.46
12.00 M.	23°.70	23°.90	39.14	35.98	39.14	35.98	1.02	0.60	0.19	0.02	12.23	12.10	336.01
Upward displacement of manometer = 0.32 mm.													336.19

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
 Rotation of original solution, 58°.9 ($t = 18^\circ$). Manometer used, No. 4.
 Rotation at conclusion of expt., 57°.7 ($t = 18^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 1°.2. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 158,550 ohms.
 Time of setting up cell, 4.30 P. M., March 23, 1906. Initial pressure, 4.30 atmospheres.

Table XVIII.

Original wt. normal concentration of solution, 0.6 Experiment No. 1.
 Rotation of original solution, $69^{\circ}.2$ ($t = 20^{\circ}$). Manometer used, No. 5.
 Rotation at conclusion of expt., $66^{\circ}.4$ ($t = 20^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^{\circ}.8$. Cell used, G.
 Calibration units of air in manometer, 442.18. Resistance of membrane, 218,000 ohms.
 Time of setting up cell, 5.00 P. M., April 10, 1906. Initial pressure, 11.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Solution.	Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
						Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.					Capillary depression.
April 10.															
7.45 P. M.	24°	30	24°	40	34.46										
April 11.															
12.00 A. M.	24°	30	24°	40	31.86		29.24	1.00	0.64	0.45	0.02	14.33	14.55	-0.22	344.82
8.30 "	24°	40	24°	10	31.74		29.16	1.00	0.64	0.45	0.02	14.37	14.55	-0.18	343.98
"	24°	40	24°	20	31.71		29.12	1.00	0.64	0.45	0.02	14.39	14.55	-0.16	343.50
11.00 "	24°	40	24°	20	31.71		29.12	1.00	0.64	0.45	0.02	14.39	14.55	-0.16	343.50
2.30 P. M.	24°	40	23°	90	31.68		29.13	1.00	0.64	0.45	0.02	14.39	14.55	-0.16	343.50

See Table XIX. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 3.78 mm.

Table XIX.

Original wt. normal concentration of solution, 0.6.
 Experiment No. 1.
 Manometer used, No. 5.
 Rotation of original solution, $69^{\circ}.2$ ($t = 20^{\circ}$).
 Capillary depression, 0.02 atmosphere.
 Rotation at conclusion of expt., $66^{\circ}.4$ ($t = 20^{\circ}$).
 Cell used, G.
 Loss in rotation, $2^{\circ}.8$.
 Resistance of membrane, 218,000 ohms.
 Calibration units of air in manometer, 442.18.
 Initial pressure, 11.80 atmospheres.
 Time of setting up cell, 5.00 P. M., April 10, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.				
April 10.													
7.45 P. M.	24° 30	24° 40	34.46										
April 11.													
12.00 A. M.	24° 30	24° 40	31.86	29.24	1.00	0.64			0.02	14.70	+0.15	336.14	
8.30 "	24° 40	24° 10	31.74	29.16	1.00	0.64			0.02	14.74	+0.19	335.35	
11.00 "	24° 40	24° 20	31.71	29.12	1.00	0.64			0.02	14.76	+0.21	334.89	
2.30 P. M.	24° 40	23° 90	31.68	29.13	1.00	0.64			0.02	14.76	+0.21	334.89	335.32

See Table XVIII.

Upward displacement of manometer = 3.78 mm.

Table XXI.

Original wt. normal concentration of solution, 0.6. Experiment No. 3.
 Rotation of original solution, $69^{\circ}.2$ ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., $67^{\circ}.4$ ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^{\circ}.8$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 272,500 ohms.
 Time of setting up cell, 12.30 P. M., April 14, 1906. Initial pressure, 9.00 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
April 14.													
4.30 P. M.	24° 10	23° 90	28.79										
7.45 "	24° 10	24° 00	28.63										
11.00 "	24° 10	24° 15	28.54	26.21	0.99	0.66	0.29	0.02	14.74	14.54	+0.20	335.00	
April 15.													
10.00 A. M.	24° 10	24° 00	28.47	26.16	0.99	0.66	0.29	0.02	14.77	14.54	+0.23	334.32	
12.30 P. M.	24° 10	23° 75	28.40	26.12	0.99	0.66	0.29	0.02	14.79	14.54	+0.25	333.87	334.32
3.00 "	24° 10	23° 70	28.41	26.14	0.99	0.66	0.29	0.02	14.78	14.54	+0.24	334.10	
5.30 "	24° 10	23° 70	28.43	26.15	1.00	0.66	0.29	0.02	14.77	14.54	+0.24	334.32	

Upward displacement of manometer = 0.64 mm.

Table XXII.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
 Rotation of original solution, $79^{\circ}.1$ ($t = 22^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of expt., $76^{\circ}.5$ ($t = 22^{\circ}$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $2^{\circ}.6$. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 222,000 ohms.
 Time of setting up cell, 5.00 P. M., March 26, 1906. Initial pressure, 9.63 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.					
March 26.															
8.15 P. M.	$23^{\circ}.35$	$23^{\circ}.60$	28.25												
March 27.															
12.00 A. M.	$23^{\circ}.35$	$23^{\circ}.45$	28.16	25.93	1.00	0.61	0.43	0.02	16.99	16.92	$+0.07$	338.39			
8.30 "	$23^{\circ}.35$	$23^{\circ}.40$	28.25	26.02	0.99	0.61	0.43	0.02	16.94	16.92	$+0.02$	339.39			
12.00 M.	$23^{\circ}.85$	$23^{\circ}.85$	28.27	26.00	0.99	0.61	0.43	0.02	16.96	16.95	$+0.01$	339.40			339.39
2.30 P. M.	$24^{\circ}.00$	$24^{\circ}.00$	28.34	26.05	0.99	0.61	0.43	0.02	16.92	16.96	-0.04	340.37			

Upward displacement of manometer = 0.24 mm.

Table XXIII.

Original wt. normal concentration of solution, 0.7.	Experiment No. 2.
Rotation of original solution, 79°.2 ($t = 19^\circ$).	Manometer used, No. 6.
Rotation at conclusion of expt., 77° ($t = 19^\circ$).	Capillary depression, 0.02 atmospheres.
Loss in rotation, 2°.2.	Cell used, G.
Calibration units of air in manometer, 402.13.	Resistance of membrane, 280,000 ohms.
Time of setting up cell, 4.30 P. M., March 30, 1906.	Initial pressure, 9.49 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.								
March 30.															
8.30 P. M.	23°.74	23°.80	24.80	22.81	0.98	0.67	0.36	0.02	16.98	16.89	+0.09	338.87			
March 31.															
12.00 A. M.	23°.74	24°.00	24.85	22.84	0.98	0.67	0.36	0.02	16.96	16.89	+0.07	339.27			
9.00 "	23°.80	24°.00	24.84	22.83	0.98	0.67	0.36	0.02	16.97	16.95	+0.02	339.14			
12.30 P. M.	24°.30	23°.90	24.94	22.89	0.98	0.67	0.36	0.02	16.92	16.98	-0.06	340.70		339.50	

Upward displacement of manometer = 0.07 mm.

Upward displacement of manometer = 0.07 mm.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
 Rotation of original solution, 79°.2 ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., 77° ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Cell used, G.
 Loss in rotation, 2°.2.
 Resistance of membrane, 280,000 ohms.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 4.30 P. M., March 30, 1906. Initial pressure, 9.49 atmospheres.

Table XXIV.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
 Rotation of original solution, 89° ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., $85^{\circ}.8$ ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $3^{\circ}.2$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 272,500 ohms.
 Time of setting up cell, 4.15 P. M., April 2, 1906. Initial pressure, 12.70 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.			
April 2.													
8.30 P. M.	23° 57	24° 30	21.74	19.96	1.01	0.67	0.53	0.02	19.30	19.35	—0.05	340.53	
11.45 "	23° 60	24° 10	21.76	19.99	1.01	0.67	0.53	0.02	19.26	19.35	—0.09	341.27	
April 3.													
8.30 A. M.	23° 60	23° 60	21.70	19.97	1.01	0.67	0.53	0.02	19.29	19.35	—0.06	340.73	340.48
12.30 P. M.	23° 60	23° 80	21.67	19.93	1.01	0.67	0.53	0.02	19.33	19.35	—0.02	340.03	
2.30 "	23° 60	24° 00	21.67	19.92	1.01	0.67	0.53	0.02	19.34	19.35	—0.01	339.85	

Upward displacement of manometer = 0.32 mm.

Table XXV.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
 Rotation of original solution, 89° ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $85^\circ.1$ ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $3^\circ.9$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 223,000 ohms.
 Time of setting up cell, 4.30 P. M., April 16, 1906. Initial pressure, 15.10 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.						
April 16.														
8.00 P. M.	23° 60	23° 50	22.93			1.01	0.67	0.64	19.09	19.36	-0.27	344.42		
11.50 "	23° 65	23° 85	21.94			1.01	0.67	0.64	19.05	19.36	-0.31	345.14		
April 17.														
9.00 A. M.	23° 70	23° 50	21.78	20.05	1.01	0.67	0.64	0.02	19.09	19.36	-0.27	344.42		
12.30 P. M.	23° 70	23° 30	21.81	20.09	1.01	0.67	0.64	0.02	19.05	19.36	-0.31	345.14		
2.30 "	23° 70	23° 30	21.69	19.98	1.01	0.67	0.64	0.02	19.17	19.36	-0.19	342.98		
5.00 "	23° 70	23° 20	21.67	19.97	1.01	0.67	0.64	0.02	19.18	19.36	-0.18	342.80		
8.00 "	23° 65	23° 10	21.68	19.99	1.01	0.67	0.64	0.02	19.16	19.36	-0.20	343.10		

See Table XXVI. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 1.8 mm.

Table XXVI.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
 Rotation of original solution, 89° ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., 85° .1 ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 3° .9. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 223,000 ohms.
 Time of setting up cell, 4.30 P. M., April 16, 1906. Initial pressure, 15.10 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.				
April 16.													
8.00 P. M.	23° 60	23° 50	22.93										
11.50 "	23° 65	23° 85	21.94										
April 17.													
9.00 A. M.	23° 70	23° 50	21.78	20.05	1.01	0.67		0.02	19.35	19.36	—0.01	339.79	
12.30 P. M.	23° 70	23° 30	21.81	20.09	1.01	0.67		0.02	19.31	19.36	—0.05	340.49	
2.30 "	23° 70	23° 30	21.69	19.98	1.01	0.67		0.02	19.43	19.36	+0.07	338.39	
5.00 "	23° 70	23° 20	21.67	19.97	1.01	0.67		0.02	19.44	19.36	+0.08	338.22	
8.00 "	23° 65	23° 10	21.68	19.99	1.01	0.67		0.02	19.42	19.36	+0.06	338.51	339.08
Due to inversion = —0.53.													
Due to dilution = +0.15.													

Due to inversion = 1.53° .
 Due to dilution = 1.53° .

See Table XXV.

Upward displacement of manometer = 1.8 mm.

Table XXVII.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
 Rotation of original solution, 98° ($t = 22^{\circ}$). Manometer used, No. 5.
 Rotation at conclusion of expt., $95^{\circ}.5$ ($t = 22^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^{\circ}.5$. Cell used, A.
 Calibration units of air in manometer, 442.18. Resistance of membrane, 64,100 ohms.
 Time of setting up cell, 1.00 P. M., May 1, 1906. Initial pressure, 10.40 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.		
May 1.													
8.00 P. M.	$24^{\circ}.00$	$24^{\circ}.50$	$24^{\circ}.50$		28.27								
May 2.													
10.30 A. M.	$24^{\circ}.00$	$24^{\circ}.20$	$24^{\circ}.20$		22.03								
6.30 P. M.	$24^{\circ}.20$	$25^{\circ}.15$	$25^{\circ}.15$		21.87								
May 3.													
10.00 A. M.	$24^{\circ}.65$	$25^{\circ}.30$	$25^{\circ}.30$		21.53	19.70	0.99	0.66	0.43	0.02	21.71	21.85	—0.14 341.81
1.00 P. M.	$24^{\circ}.70$	$25^{\circ}.30$	$25^{\circ}.30$		21.50	19.67	0.99	0.66	0.43	0.02	21.73	21.85	—0.12 341.55
5.30 "	$24^{\circ}.80$	$25^{\circ}.30$	$25^{\circ}.30$		21.43	19.61	0.99	0.66	0.43	0.02	21.81	21.86	—0.05 340.41
11.00 "	$24^{\circ}.90$	$25^{\circ}.35$	$25^{\circ}.35$		21.35	19.37	0.99	0.66	6.43	0.02	21.90	21.87	+0.03 339.12
May 4.													340.19
10.30 A. M.	$24^{\circ}.90$	$24^{\circ}.50$	$24^{\circ}.50$		21.22	19.32	0.99	0.66	0.43	0.02	21.97	21.87	+0.10 338.04

Upward displacement of manometer = 1.21 mm.

Table XXVIII.

Original wt. normal concentration of solution, 0.9.	Experiment No. 2.
Rotation of original solution, 98° ($t = 22^\circ$).	Manometer used, No. 6.
Rotation at conclusion of expt., 95°.6 ($t = 22^\circ$).	Capillary depression, 0.02 atmosphere.
Loss in rotation, 2°.4.	Cell used, B.
Calibration units of air in manometer, 402.13.	Resistance of membrane, 84,000 ohms.
Time of setting up cell, 12.30 P. M., May 1, 1906.	Initial pressure, 14.00 atmospheres.

Upward displacement of manometer = 0.87 mm.

Original wt. normal concentration of solution, 0.9.
 Experiment No. 2.
 Manometer used, No. 6.
 Rotation of original solution, 98° ($t = 22^\circ$).
 Capillary depression, 0.02 atmosphere.
 Rotation at conclusion of expt., 95° 6 ($t = 22^\circ$).
 Cell used, B.
 Loss in rotation, 2° 4.
 Resistance of membrane, 84,000 ohms.
 Calibration units of air in manometer, 402.13.
 Initial pressure, 14.00 atmospheres.
 Time of setting up cell, 12.30 P. M., May 1, 1906.

Table XXIX.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
 Rotation of original solution, $107^{\circ}.2$ ($t = 22^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., $104^{\circ}.8$ ($t = 22^{\circ}$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $2^{\circ}.4$. Cell used, B.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 99,100 ohms.
 Time of setting up cell, 1.00 P. M., April 27, 1906. Initial pressure, 14.60 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.						Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.						
April 28.															
7.30 P. M.	23° .40	24° .70	18.40												
April 29.															
12.00 A. M.	23° .50	24° .75	17.69												
9.30 "	23° .60	23° .20	17.41	16.04	1.00	0.67	0.41	0.02	24.34	24.19	+0.15	337.63			
1.00 P. M.	23° .55	23° .30	17.38	16.01	1.00	0.67	0.41	0.02	24.40	24.19	+0.21	336.66			
7.00 "	23° .55	23° .30	17.37	16.00	1.00	0.67	0.41	0.02	24.41	24.19	+0.22	336.52			336.39
April 30.															
12.00 A. M.	23° .55	23° .30	17.33	15.97	1.00	0.67	0.41	0.02	24.47	24.19	+0.28	335.70			
9.00 "	23° .57	23° .93	17.35	15.95	1.00	0.67	0.41	0.02	24.49	24.19	+0.30	335.45			

Upward displacement of manometer = 0.88 mm.

Table XXX.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.
 Rotation of original solution, $107^{\circ}.4$ ($t = 18^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., $103^{\circ}.4$ ($t = 18^{\circ}$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, 4° . Cell used, B.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 84,000 ohms.
 Time of setting up cell, 3.00 P. M., May 7, 1906. Initial pressure, 17.00 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.					
May 8.														
12.00 A. M.	24° 90	24° 50	21.05											
10.30 "	24° 70	23° 40	20.50											
7.30 P. M.	24° 60	23° 90	18.15											
11.30 "	24° 60	24° 50	18.17											
May 9.														
10.15 A. M.	24° 60	24° 14	18.07	16.60	1.00	0.67	Due to inversion = -0.41.	0.02	23.88	24.28	-0.40	345.22	342.72	
2.00 P. M.	24° 60	24° 20	18.00	16.53	1.00	0.67	Due to dilution = +0.37.	0.02	23.94	24.28	-0.34	344.35		
6.00 "	24° 60	24° 20	18.01	16.54	1.00	0.67		0.02	23.96	24.28	-0.32	344.07		
May 10.														
12.00 A. M.	24° 60	24° 10	17.94	16.48	1.00	0.67		0.02	24.05	24.28	-0.23	342.78	342.72	
9.00 "	24° 50	23° 90	17.93	16.49	1.00	0.67		0.02	24.05	24.28	-0.22	342.66		

Upward displacement of manometer = 2.97 mm.

Upward displacement of manometer = 2.97 mm.

Due to inversion = -0.41.
 Due to dilution = +0.37.

Table XXXI.—Summary of Conditions.

Weight-normal concentration.	No. of experiment.	Cell used.	Resistance.	Initial pressure. Atmospheres.	Length of time in reaching maximum pressure. Hours.	Length of time cell remained in bath. Hours.	Change of temperature of bath during the experiment.	Time over which the change of temperature extended. Hours.
0.1	1	G	350,000	2.10	7.00	23.00	0°.10	14.0
	2	"	275,000	2.20	7.00	19.50	0°.05	11.0
0.2	1	"	271,250	1.98	11.00	33.80	0°.50	22.0
	2	"	280,000	2.30	18.00(?)	41.75	0°.54	24.0
	3	"	225,000	2.13	8.00	17.75	0°.20	10.0
0.3	1	"	275,000	3.50	7.75	23.50	0°.10	11.0
	2	"	273,250	3.40	8.00	22.25	0°.40	14.0
0.4	1	"	372,300	6.80	8.50	24.50	0°.27	16.0
	2	"	277,500	4.30	6.75	19.25	0°.10	12.0
0.5	1	"	274,500	10.80	7.00	19.00	0°.20	3.5
	2	"	158,550	4.30	7.50	19.50	0°.00	
0.6	1	"	218,000	11.80	7.00	21.50	0°.10	14.0
	2	"	215,000	10.45	7.00	21.75	0°.15	15.0
	3	"	272,500	9.00	10.50	17.00	0°.00	
0.7	1	"	222,000	9.63	7.00	21.50	0°.65	26.0
	2	"	280,000	9.49	4.00	20.00	0°.56	12.0
0.8	1	"	272,500	12.00	4.25	22.25	0°.03	3.0
	2	"	223,000	15.10	16.50(?)	27.50	0°.05	3.0
0.9	1	A	64,100	10.40	45.00(!)	79.50	0°.25	13.0
	2	B	84,000	14.00	45.50(!)	58.50	0°.25	13.0
1.0	1	"	99,100	14.60	44.50(!)	68.00	0°.05	3.5
	2	"	84,000	17.00	43.20(!)	66.00	0°.10	9.0
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Osmotic Pressure of Cane Sugar Solutions.

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Weight-normal concentration.	No. of experiment.	Maximum and minimum temperatures of solution.	Observed osmotic pressure.	Theoretical gas pressure at same temperature.	Maximum and minimum differences between osmotic and gas pressures.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24° 0	2.51	2.42	+0.09, +0.11	327.85	325.21
	2	24° 2	2.55	2.43	+0.11, +0.14	322.56	
0.2	1	20° 65	4.72	4.79	-0.06, -0.09	344.96	341.87
	2	21° 2	4.78	4.80	+0.01, -0.04	340.90	
	3	21° 65	4.81	4.81	0.00, -0.01	339.74	
0.3	1	21° 6	7.24	7.21	+0.02, +0.04	338.37	338.29
	2	19° 7	7.20	7.16	0.00, +0.05	338.20	
0.4	1	21° 48	9.64	9.61	+0.01, +0.04	338.73	338.12
	2	22° 1	9.69	9.63	+0.06, +0.06	337.50	
0.5	1	22° 5	12.06	12.06	+0.01, -0.02	339.59	337.89
	2	23° 7	12.22	12.10	+0.09, +0.15	336.19	
0.6	1	24° 3	14.74	14.55	+0.15, +0.21	335.32	335.24
	2	24° 15	14.70	14.55	+0.15, +0.16	336.07	
	3	24° 1	14.77	14.54	+0.20, +0.25	334.32	
0.7	1	23° 35	16.95	16.94	-0.04, +0.07	339.59	339.55
	2	23° 75	16.96	16.93	+0.02, +0.09	339.50	
0.8	1	23° 57	19.30	19.35	-0.01, -0.09	340.48	339.78
	2	23° 65	19.39	19.36	-0.05, +0.07	339.08	
0.9	1	24° 65	21.82	21.86	-0.14, +0.10	340.19	339.51
	2	24° 65	21.91	21.86	+0.01, +0.11	338.82	
1.0	1	23° 55	24.42	24.19	+0.15, +0.30	336.39	339.56 ⁽⁸⁾
	2	24° 5	24.05	24.28	-0.22, -0.23 ⁽⁵⁾	342.72 ⁽⁷⁾	

Theoretical molecular weight of cane sugar = 339.60.

Mean molecular weight of cane sugar calculated from the observed osmotic pressure of all concentrations = 337.59.

the conclusion was reached that the potters were not likely to solve the problem of cell-making. A, though still serviceable, has deteriorated in the course of time in respect to the maximum resistance of its membrane, which, in the beginning, was usually over 100,000 ohms. B, on the other hand, now exhibits a higher resistance than formerly.

The conduct of the three cells, G, A and B, with respect to the time required for the development of maximum pressure (see column 6, Table XXXI.), is also noteworthy. In G the solutions usually developed their maximum pressures within 7 hours, while in A and B over 40 hours were required for the same purpose. Both A and B have deteriorated in this respect. In general, it may be said that the interval between the time of setting up A or B and that of the first reading which is made the basis of a calculation of pressure, is now nearly twice as long as formerly. It appears, from the figures in column 6, that in G the solutions differed greatly in regard to the time consumed in reaching the highest pressures. In this respect the figures are somewhat misleading. They really give the time which elapsed between the placing of the cell in the bath and the taking of the first reading *after* an approximately maximum pressure had been reached, and in several instances the first formal reading was probably long after the solution had developed its maximum pressure.

Attention is called to the fact that the time within which the highest pressure is developed appears to be wholly independent of the concentration of the solution.

Column 8, Table XXXI., gives the maximum changes of temperature of the water—and, consequently of the solutions while the cells were in the bath, and column 9 gives the time over which these changes extended, *i. e.*, the time interval between the highest and lowest temperatures of the bath. The greatest change of temperature during an experiment was $0^{\circ}.65$, but, as this was gradual and extended over 26 hours, no "thermometer effects" were to be feared. On three other occasions the changes of temperature equalled or exceeded $0^{\circ}.5$. These variations ($0^{\circ}.65$, $0^{\circ}.56$, $0^{\circ}.54$ and $0^{\circ}.5$) are unnecessarily large under our present conditions, and they were

due, in each case, to a neglect of some of the arrangements by means of which we seek to maintain approximately constant temperatures in the bath while an experiment is in progress.

2. Table XXXII. *Summary of Results.* The method by which some of the values given in this table have been computed requires explanation.

Column 3 gives the lowest and highest temperatures of the water-bath during the several experiments. It is the differences between these which appear in column 8 of Table XXXI. The solutions in the cells are presumed to have the same temperatures as the water in the bath.

The values given in column 4, under the head of "Observed osmotic pressure," are *mean* values and they have been computed by adding the quantities given under "Osmotic pressure corrected," Tables IV. to XXX., and dividing the sum by the number of recorded observations. They represent quite exactly the mean, experimentally determined, osmotic pressure of the various solutions at the mean of the temperatures recorded in column 3.

The corresponding theoretical gas pressures, at the same temperatures, are given in column 5. These, like the "observed osmotic pressures" in column 4, are mean values which have been computed from the data given under "theoretical gas pressure" in Tables IV. to XXX.

In column 6 appear the minimum and maximum differences, for each concentration, between the observed osmotic pressure and the theoretical gas pressure. They are taken from the columns which are designated in Tables IV. to XXX. by the title "difference between pressure found and calculated," and are not mean values.

In connection with the molecular weights calculated from the observed osmotic pressure (columns 7 and 8), attention is called to the fact that, with one exception, they are much nearer to the theoretical value than are those which we are accustomed to obtain by the other so-called physical methods. The exception referred to is the case of the 0.1 weight-normal solution. The molecular weights found in this instance were 327.85 and 322.56, with a mean value of 325.21, which differs

from the theoretical molecular weight of cane sugar (339.6) by 14.39 units, or 4.26 per cent. No good reason is known for excluding that determination, and it is given with the others, notwithstanding the fact that much better results for the same concentration were obtained last year—namely, 337.0 and 336.6.

The effect of a given error in the measurement of osmotic pressure upon the computed molecular weights varies inversely as the concentrations of the solutions. This is made apparent by the following table, which gives, for each concentration, the effect in units, at 20°, of an error of 0.1 atmosphere upon the estimated molecular weight of cane sugar :

Weight-normal concentration.	Effect of 0.1 atmosphere upon molecular weight. Units.
0.1	14.21
0.2	7.11
0.3	4.74
0.4	3.55
0.5	2.84
0.6	2.37
0.7	2.03
0.8	1.78
0.9	1.57
1.0	1.42

It will be seen from the foregoing table that extreme care is necessary in order to obtain good molecular weight determinations by measuring the osmotic pressure of dilute solutions.

The difficulty which is peculiar to the measurement of the pressures of concentrated solutions is the large effect of small errors of calibration, or of reading, or of correction for meniscus. This will be illustrated by reference to Table XXXII. It will there be seen (column 6) that in the case of the two determinations of the osmotic pressure of weight-normal solutions the maximum deviations of observed from theoretical values were +0.3 atmosphere (No. 1) and -0.23 atmosphere (No. 2). These deviations, though seemingly large, are just about equivalent to the errors of meniscus in these measurements.

Our results are presented in their final form in Table

XXXIII., which differs from Table XXXII. only in that the extremes of temperature values (column 3, XXXII.) have been averaged and the extreme deviations of osmotic from gas pressure (column 6, XXXII.) have been replaced by the differences between the mean observed osmotic pressure and the mean calculated gas pressure.

If the mean of all the results is taken, the molecular weight of cane sugar is found to be 337.59, which differs from the theoretical value (339.6) by 2.01 units, or 0.59 per cent.

If the results obtained by the measurement of the pressure of the 0.1 weight-normal solution are excluded, and the mean of the remainder is taken, the molecular weight is found to be 338.82, which differs from the theoretical value by 0.78 unit, or 0.23 per cent.

These results are probably as precise as we can hope to obtain under present conditions. In our judgment they suffice to establish the conclusion which was deduced from the earlier series of measurements, namely, that *cane sugar in aqueous solution exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature, and the volume of the gas were reduced to that of the solvent in the pure state.*

It will be shown later that the same conclusion holds good for glucose.

For the present it must remain undecided whether the standard for the *volume of the solvent in the pure state* is its volume at maximum density, or at the prevailing temperature. This problem cannot be solved by the measurement of the osmotic pressure of cane sugar solutions, owing to the magnitude of the uncertainties which are due to inversion. If a substance can be found which undergoes no chemical change in the cell, and whose concentration of solution can be accurately ascertained, the question as to which volume of the solvent is the correct one for comparison can be answered; for, with such a substance, measurements of osmotic pressure could be made with a precision nearly equal to that which is required of an atomic weight determination.

It is hoped that we may be able, later, to extend the work upon cane sugar by taking up the measurement of pressure in

Table XXXIII.—Final Summary of Results.

Weight-normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Differences between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24°.05	2.51	2.42	+0.09	327.85	
	2	24°.23	2.55	2.43	+0.12	322.56	325.21
0.2	1	20°.90	4.72	4.79	-0.07	344.96	
	2	21°.47	4.78	4.80	-0.02	340.90	
	3	21°.75	4.81	4.81	0.00	339.74	341.87
0.3	1	21°.65	7.24	7.21	+0.03	338.37	
	2	19°.90	7.20	7.16	+0.04	338.20	338.29
0.4	1	21°.62	9.64	9.61	+0.03	338.73	
	2	22°.15	9.69	9.63	+0.06	337.50	338.12
0.5	1	22°.60	12.06	12.06	0.00	339.59	
	2	23°.70	12.22	12.10	+0.12	336.19	337.89
0.6	1	24°.35	14.74	14.55	+0.19	335.32	
	2	24°.23	14.70	14.55	+0.15	336.07	
	3	24°.1	14.77	14.54	+0.23	334.32	335.24
0.7	1	23°.68	16.95	16.94	-0.01	339.59	
	2	24°.03	16.96	16.93	+0.03	339.50	339.55
0.8	1	23°.59	19.30	19.35	-0.05	340.48	
	2	23°.68	19.39	19.36	+0.03	339.08	339.78
0.9	1	24°.78	21.82	21.86	-0.04	340.19	
	2	24°.78	21.91	21.86	+0.05	338.82	339.51
1.0	1	23°.58	24.42	24.19	+0.23	336.39	
	2	24°.55	24.05	24.28	-0.23	342.72	339.56
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)

the vicinity of 0° , and also that of more concentrated solutions.

The Depression of the Freezing Points of Cane Sugar Solutions.

In the earlier communication¹ attention was called to the fact that if the factor of density is taken into account, the apparent abnormality of the freezing points of cane sugar solutions disappears, in the sense that all concentrations of solution then conform to a general rule. The rule was formulated as follows: If Δ_1 represents the calculated depression of the freezing point, Δ its observed value, D the density of the solution at the temperature of freezing, and N its weight-normal concentration, then

$$\Delta_1 = 1.85 N D = \Delta \text{ for all concentrations.}$$

The rule was found to hold for all concentrations up to that of a gram-molecular weight of sugar dissolved in 1,000 grams of water; but, as the results upon which it was based were somewhat hastily obtained, and since the thermometer which was used had not been tested as to its accuracy, it was thought desirable to repeat the work with greater care and under more favorable conditions. This has been done.

The thermometer used in the later work is graduated in $0^{\circ}.01$ from $+1^{\circ}.0$ to $-5^{\circ}.0$, and its errors have been determined at the "*Reichsanstalt*." Before employing the instrument, it was tested as to a possible continued shrinkage of the bulb. It was found that the 0° point had suffered an upward displacement, amounting to $0^{\circ}.02$, since the date of the *Reichsanstalt's* certificate, which, of course, was taken into account in applying corrections for the certified errors of the thermometer.

The densities of the solutions were determined in pycnometers, which were modified somewhat in form, to enable us to ascertain with a fair degree of certainty the temperature of minimum volume.

We cannot predict *which density* of solutions, if any, will be found to have a definite relation to their freezing points; accordingly, the specific gravities of the cane sugar solutions

¹ THIS JOURNAL, 34, 93.

were determined: (1) at the freezing point of the solvent, *i. e.*, 0° , (2) at the freezing temperature of the solution, and (3), as far as practicable, at the temperature of minimum volume, *i. e.*, maximum density.

No great degree of accuracy can be ascribed to the determinations of temperatures of maximum density, though they are believed to be fairly correct. The greatest difficulty which was experienced in this connection was due to the fact that, in the case of the 0.5 normal, and of more concentrated solutions, the temperature of maximum density is considerably below that of freezing. On this account great caution was necessary, in some instances, in order to secure the requisite amount of undercooling before the formation of ice set in. In the case of the normal solution it could not be done, and the temperature of minimum volume of that concentration could only be conjectured from the values which had been obtained for less concentrated solutions.

The data which were gathered in the course of the work upon the densities and the freezing-points of cane sugar solutions are brought together in the following tables. For the present, they serve no very obvious purpose except to confirm the rule for cane sugar which was expressed by the equation $\Delta_1 = 1.85 \text{ N D} = \Delta$. It appears to the authors desirable to ascertain *experimentally* (rather than by an exercise of the speculative faculty) whether the same or any other definite relation exists between the densities and the so-called *abnormal freezing points* of other solutions. The rule does not hold good for glucose, but the freezing points of glucose solutions are *normal* in the sense that the magnitude of the depression is strictly proportional to the weight-normal concentration.

If the densities of solutions which exhibit abnormalities of freezing points are found to be connected in some definite way with those abnormalities, it requires no great exercise of the imagination to predict that a similar relation will be found to hold between the vapor tension and the densities of the same solutions, but the normal procedure would seem to be, first to establish the fact, and then to seek for the reason.

Table XXXIV.—Density of Cane Sugar Solutions.

Weight-normal concentration.	Temperature of maximum density.	Density at temperature of minimum volume.	Density at freezing point of the solution.	Density at freezing point of the solution.
0.1	+4°.2	1.01310	1.01310	1.01309
0.2	+3°.2	1.02570	not determined	1.02574
0.3	+1°.0	1.03787		1.03787
0.4	—0°.4	1.04953		1.04951
0.5	—1°.9	1.06079	1.07139	1.06067
0.6	—3°.7	1.07160	1.08180	1.07136
0.7	—5°.0	1.08204	1.09163	1.08167
0.8	—6°.0	1.09204	1.10116	1.09156
0.9	—7°.5	1.10175	1.11056	1.10107
1.0	not determined	1.11114 ¹		1.11025

Table XXXV.—Observed and Calculated Freezing Points of Cane Sugar Solutions.

Weight-normal concentration.	Observed depression of the freezing point.	Calculated values of 1.85 ND. ²	Difference between actual and calculated depression.	Molecular lowering of freezing points.
0.1	0°.195	0°.187	0°.008	1°.95
0.2	0°.393	0°.380	0°.013	1°.96
0.3	0°.584	0°.576	0°.008	1°.95
0.4	0°.784	0°.777	0°.007	1°.96
0.5	0°.983	0°.981	0°.002	1°.97
0.6	1°.190	1°.189	0°.001	1°.98
0.7	1°.390	1°.401	—0°.011	1°.99
0.8	1°.621	1°.616	0°.005	2°.02
0.9	1°.829	1°.834	—0°.005	2°.03
1.0	2°.066	2°.056	0°.010	2°.07

It is customary at the present time to ascribe the abnormally great depression of the freezing points of certain concentrated solutions to an appropriation, by the dissolved substance, of a portion of the solvent, which is attended (if it really occurs) by a corresponding concentration of the solution. In this way the eccentricities of the freezing points of cane sugar solutions have been explained; but the authors feel called upon to point out one fact which is not easily reconciled with this explanation, namely, the fact that there are no corresponding irregularities in the *osmotic pressures* of cane sugar solutions. Within the limits of unavoidable experimental errors, the os-

¹ Calculated.² Density at minimum volume.

otic pressures of cane sugar solutions have been found to be proportional to their supposed concentrations, which could hardly be the case if the sugar had abstracted from the solvent the quantities of water necessary to account for the aberrations of the freezing points.

The depression of the freezing-point of a 0.1 weight-normal solution of cane sugar is $0^{\circ}.195$, while that of the normal solution is $2^{\circ}.066$ instead of $1^{\circ}.95$. In other words, the depression of the freezing-point of the weight-normal solution is *abnormal* to an extent not less than $0^{\circ}.116$, the equivalent of which, in osmotic pressure at 24° , is approximately 1.44 atmospheres. If, then, the sugar in a weight-normal solution withdraws enough water from the solvent to produce an abnormal depression of the freezing point amounting to $0^{\circ}.116$, we should have found, for that concentration, an osmotic pressure of 25.67 atmospheres instead of 24.23 atmospheres, which is the mean value of all our determinations, with a maximum deviation from this value, among the individual determinations, amounting to about 0.25 atmosphere. These figures, since they represent mean values, are not exact, but they are correct to within 0.02 or 0.03 of an atmosphere.

It may be surmised that, at the comparatively high temperatures at which our measurements were made, the *whole* of the water does in reality play the part of solvent, while, at lower temperatures, a portion of it is appropriated by the sugar, giving rise to a concentration of the solution and, consequently, to an abnormal depression of the freezing point.

While, in general, we would deprecate free speculation until after many more facts relating to osmotic pressure have been *experimentally* established, this provisional reconciliation of the contradictions between freezing point depressions on the one hand, and osmotic pressure on the other, appears to have in it enough of plausibility to make desirable a determination of the osmotic pressure of cane sugar solutions at *low* temperatures, and this will be undertaken in the near future. If the supposed abstraction of water from the solvent takes place within the range of low temperatures at which we find it practicable

to work, we may expect to find evidence of it in the form of abnormally high osmotic pressures.

JOHNS HOPKINS UNIVERSITY,
May 25, 1906.

REPORTS.

The Change of Oxygen into Ozone at a High Temperature, and the Oxidation of Nitrogen.

Under this title Franz Fischer and Fritz Braehmer have recently published an interesting article,¹ of which the following is an abstract :

Ozone, like nitric oxide and hydrogen peroxide, is an endothermic compound, it should, therefore, be readily formed at high temperatures and should be stable at its temperature of formation.

The conditions for the production of nitric oxide from the air are known.² Nernst³ has calculated the concentration-equilibrium for different temperatures.

Table I.— $N_2 + O_2 \rightleftharpoons 2NO$.

T(absol.).	$\theta = ^\circ C.$	NO observed.	NO calculated.
1811	1538	0.37 vol. per cent	0.35
2033	1760	0.64	0.67
2195	1922	0.97	0.98
3200	2927	5.00 approx.	4.4

The speed of formation is relatively slow. Nernst has computed the following values for the time in which one-half of the possible nitric oxide concentration occurs when air is heated : At 1200° very long ; 1538° , 97 seconds ; 1737° , 3.5 seconds ; 2600° , 0.0018 seconds. As the speed of decomposition corresponds to the speed of formation, the possibility of cooling the NO to lower temperatures without especial precaution is apparent.

Moritz Traube⁴ formed hydrogen peroxide at high temperatures by directing a jet of burning hydrogen on water or ice, the sudden cooling preserving the peroxide intact and enabling him to isolate it from the mixture of hydrogen, oxygen, water and hydrogen peroxide existing at 2400° .

¹ Ber. d. chem. Ges., 39, 941 (1906).

² Vide Brode's Monograph, "Oxidation des Stickstoffs in der Hochspannungsflamme," von Johannes Brode, Halle : Knapp, 1905, and a recent report in this JOURNAL "On the Oxidation of Atmospheric Nitrogen." THIS JOURNAL, 35, 358.

³ Nernst : Nachr. kön. Gesell. Wiss. Göttingen, 1904, 261.

⁴ Ber. d. chem. Ges., 18, 1890.

The following table contains Nernst's¹ calculations for the percentage of hydrogen peroxide which can co-exist with water vapor and oxygen at given temperatures and 0.1 atmosphere pressure :

Table II.— $2H_2O + O_2 \rightleftharpoons 2H_2O_2$.

T (absol.).	$\theta = ^\circ C.$	Per cent H_2O_2 .
2784	2511	0.66
2154	1881	0.24
1493	1220	0.028
1140	867	0.0032
923	650	0.00036

As the temperature of the hydrogen flame is much above 2000° it must contain hydrogen peroxide, and Traube found experimentally 0.74 per cent.

The values which Nernst² has calculated for the speed of decomposition of hydrogen peroxide are very close to those which were determined by Clement for ozone.

In the following table Nernst gives the figures calculated for the percentage of ozone, which can exist in equilibrium with oxygen at different temperatures :

Table III.— $3O_2 \rightleftharpoons 2O_3$.

T (absol.).	$\theta = ^\circ C.$	Vol. per cent O_3 .	Weight per cent O_3 .
1569	1296	0.1	0.15
2321	2048	1.0	1.52
4773	4500	10.0	16.50

Clement found that at given temperatures the speed of decomposition of ozone is several million times greater than that of nitric oxide, while at 1000° an ozone-oxygen mixture, containing 1 per cent of ozone, drops to 0.001 per cent in 0.0007 second ; the speed of decomposition of nitric oxide at that temperature is very small.

To sum up, we see that for nitric oxide and hydrogen peroxide theory and experiment agree qualitatively, for nitric oxide quantitatively.

As to the formation of ozone at high temperatures, it had not been experimentally proved before the present work ; for though many chemists, among whom were Schönbein, Böttger, Struve and Traube, believed that they detected the odor of ozone when hydrogen burned, other chemists denied this and said that the odor and reactions were due to oxides of ni-

¹ Z. physik. Chem., 46, 722.

² Z. elek. Chem., 11, 713.

trogen or to hydrogen peroxide. Other experimenters thought that they detected the odor of ozone when air or oxygen was passed over glowing platinum.

Clement,¹ in his second series of experiments, found that under the conditions at which previous observers had worked, ozone could not be detected, but nitric oxide or nitrous anhydride was obtained, which, in great dilution, has the odor of ozone and acts in the same way on most reagents. Clement used Arnold and Mengel's² "tetra-base" paper, *i. e.*, paper soaked in an alcoholic solution of tetramethylpara₄diaminodiphenylmethane. Ozone colors this paper violet, nitric oxides pale yellow, while hydrogen peroxide does not affect it. Clement also worked with Nernst filaments at 3000° and could detect no ozone. In short, the only case where he did detect it was in the action of electric sparks on air, but in this instance it is probable that the ozone was formed by the action of the ultra-violet rays from the spark and not by thermal action.

From the facts thus far enumerated, Fischer and Braehmer concluded that to obtain ozone from heated oxygen one must cool the heated gas more quickly than the ozone could decompose.

They have accomplished this by heating oxygen in various ways in *liquid oxygen* or *liquid air*. The oxygen may be heated by burning hydrogen or other gases, by a glowing object, or by sparks, as detailed below.

The apparatus used in burning hydrogen in liquid air or oxygen is shown in Fig. I. It consists of a test tube 18x4 cm., closed with a cork stopper. In the cork are three tubes; the bent tube *a* is to conduct the outflow of gas into water; the tube *b* is for filling the apparatus with liquid air or liquid oxygen. The tube *c*, through which the hydrogen is introduced, is prolonged by a quartz tube 10 cm. long, reaching nearly to the bottom of the test tube; the test tube is placed in a Dewar bulb. For an experiment both the unstoppered test tube and Dewar bulb are filled with pure liquid air, the test tube being two-thirds full. A current of pure, dry hydrogen is passed through tube *c* and ignited; the current is so regulated that the flame is about 1 cm. long; now the hydrogen flame is plunged into the test tube of liquid air till the cork fits tightly; the flame burning in the liquid air causes the latter to boil away rapidly; in 2-3 minutes it nearly boils out of the tube; the flame is withdrawn from the tube before it is exposed by the liquid boiling away.

The gas escaping from the tube through *a* had the odor of

¹ Ann. Phys., 14, 334.

² Ber. d. chem. Ges., 25, 1324.

ozone, but gave no ozone reactions ; the surface of the liquid air remaining in the tube was covered with a bluish snow ; on

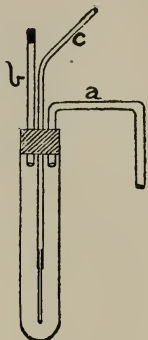


Fig. I.

filtering, it remained on the filter and was proved to be frozen nitric oxide ; the characteristic and delicate test for hydrogen peroxide with titanous acid failed to show any trace of this substance. The filtrate was poured into a porcelain crucible and allowed to boil away ; a strong odor of ozone was noticeable, "tetra-base" paper held over the crucible turned violet, and as the last of the air boiled off, dark blue rings of pure liquid ozone were left.

Control experiments, made by boiling off liquid air alone showed that the liquid air used contained no trace of ozone.

The experiment proves that nitric oxide and ozone, but no hydrogen peroxide, are formed when hydrogen is burned in liquid air, and that, by rapid cooling, it is possible to preserve the ozone dissolved in the liquid air, and easily separate it from the frozen oxides of nitrogen. While only NO is formed at high temperatures, on cooling—through oxidation—mixtures of gaseous NO and NO₂ would result, yielding, at a low temperature, solid N₂O₃.¹

The following substances were burned in—or in contact with—liquid air :

Carbon monoxide : Yield, solid carbon dioxide, solid nitrous anhydride, liquid ozone.

Acetylene : Yield, carbon, carbon dioxide, nitrous anhydride and ice as solids, liquid ozone.

¹ THIS JOURNAL, 35, 358.

Hydrogen sulphide : Yield, hydrogen sulphide, sulphur dioxide, water as solids, traces of liquid ozone.

Burning sulphur : Yield, sulphur dioxide, nitrous anhydride as solids, liquid ozone.

Glowing charcoal : Yield, carbon dioxide, nitrous anhydride as solids, liquid ozone.

Glowing splinter of wood : Yield, carbon, carbon dioxide, nitrous anhydride and water as solids, liquid ozone.

In none of these reactions was hydrogen peroxide formed.

Hydrogen burned in pure, liquefied, electrolytic oxygen, in an apparatus arranged to exclude air, yielded ozone only.

Another portion of the same oxygen was boiled off and was proved to contain no ozone.

A platinum wire heated by an electric current was plunged into liquid air ; as soon as the layer of gaseous air (Leidenfrost phenomenon) had formed around the wire, the latter became white-hot, indicating a temperature of about 1700° ; only ozone was formed.

This experiment proves that, at temperatures below the melting point of platinum, nitric oxide is not formed from liquid air, while ozone is produced.

A Nernst filament, heated by a current of 0.5 ampere and 220 volts, plunged in liquid air or in liquid oxygen, yielded ozone only ; here, as with the platinum wire, the temperature was not high enough for nitric oxide to form.

On arranging an apparatus so that an arc was formed between platinized copper terminals in liquid air, solid oxide of nitrogen and liquid ozone were produced.

The ozone formed by the arc exploded ; that formed by the platinum wire or Nernst filament was not explosive. The authors ascribe the explosiveness of ozone, therefore, to traces of oxides of nitrogen dissolved in it.

The formation of nitric oxide, as already proved by others, is purely thermal ; the formation of ozone is generally thermal, though in case of the arc and still more in case of sparks, it is probable that the photochemical action of the ultraviolet light has a large share in its production.

To determine whether heat or light caused the action when the Nernst filament was used, the following two experiments were performed. 1. A Nernst filament was put in a closed quartz tube, the pressure in the tube reduced to 12 mm., the current turned on, and the tube containing the glowing filament plunged into liquid air in an apparatus similar to that in Fig. I. The air boiled gently but no ozone was formed in the liquid air ; that ozone is formed if enough heat passes through

the quartz is proved by Experiment 2, in which a quartz U-tube was filled with hydrogen at 3 mm. pressure and the discharge from a small induction coil passed through it; when it was plunged into the liquid air ozone was at once formed outside the quartz tube, as a part of the short wave heat rays, produced within the tube, passed through the quartz and ozonized the oxygen. In the first experiment the heat rays from the glowing filament had to pass through an air cushion of 12 mm. pressure and 0.5 cm. thickness, hence did not pass through the quartz. Warburg and Regener¹ have shown that ozonizing light rays are not readily absorbed by air or oxygen, so that if the ozonization by the glowing Nernst filament depended entirely, or in part, on ozonizing light rays, ozone should have been formed in Experiment 1.

It is well known that hydrogen peroxide is produced by rapidly cooling the products of combustion of hydrogen; yet the authors found no trace of hydrogen peroxide after burning hydrogen in liquid air or in liquid oxygen; they suggest the following explanation: The formation of ozone, of nitric oxide and of hydrogen peroxide, must be preceded by a dissociation of molecular oxygen, $O_2 \rightleftharpoons O + O$. The speed of reaction in the formation of ozone and hydrogen peroxide being approximately equal, in the experiments in liquid air or oxygen, where combustion occurs in presence of a large excess of oxygen, many more molecules of oxygen will be oxidized to ozone than water molecules to hydrogen peroxide. Further, in the moment of cooling, ozone may react on hydrogen peroxide, $O_3 + H_2O_2 = H_2O + 2O_2$, thus using up the relatively small amounts of hydrogen peroxide formed.

The authors studied the quantitative relations of the ozone formation, choosing as their method the action of the Nernst filament on liquid oxygen. The apparatus is shown in Fig. II. The Nernst filament is horizontal between the ends of the electrodes; the capillary tube A dips into mercury. About 30 cc. of pure liquid oxygen are put in the test tube; as soon as the tube is closed by the glass stopper carrying the electrodes and glowing Nernst filament, oxygen begins to escape through the capillary tube; but a Dewar bulb B, filled with liquid air, is instantly placed around the test tube, thus cooling the liquid oxygen below its boiling point so that none can escape. On the contrary, there was a diminution of pressure equivalent to 250 mm. of mercury.

In four experiments the Nernst filament was kept 25, 50, 125 and 360 minutes, respectively, in the liquid oxygen. The

¹ Sitzungsber. k. preuss. Akad. Wiss., 1904, p. 1228.

ozone formed was determined by changing the glass stopper for one carrying a tube connecting with an absorption appa-

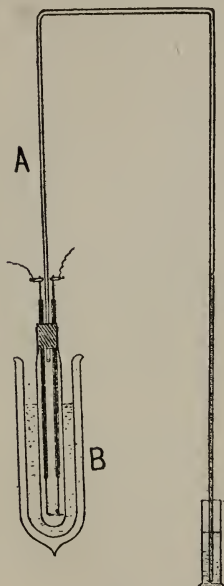


Fig. II.

tus filled with potassium iodide solution; the ozone solution was allowed to boil off, the gasified ozone swept out by a current of compressed air, and the iodine set free was determined. The following table gives the results:

Time. Minutes.	Mg. O ₃ .	Solution vol. cc.	Solution. Grams.	Weight per cent O ₃ .
25	40	30	33.6	0.12
50	76	32	35.8	0.21
125	159	30	33.6	0.47
360	322	30	33.6	0.96

If a curve is plotted using the time in minutes as abscissae and the percentages of ozone as ordinates, a glance at the figures shows that the percentage of ozone formed does not in-

crease with the time, but much more slowly ; a stationary condition had not been reached in 360 minutes, which is the limit of the authors' experimental data, but their study of the curve leads them to believe that an ozone-oxygen equilibrium is reached at 1.5 per cent, *i. e.*, that the ozone concentration will not increase beyond 1.5 per cent at the temperature of the Nernst filament.

On comparing these figures with those calculated by Nernst in Table III., assuming that the Nernst filament gave a temperature of 2048°, which is probably about correct, and assuming that the maximal concentration which the authors calculate by graphic extrapolation of their curve is accurate, there is close agreement between the experimental result and Nernst's figures, which give the absolute temperatures calculated from the electromotive energy of the ozone-oxygen couple for different relations of concentration of oxygen to ozone.

The authors calculate that by this method 3.5 grams of a 0.12 solution of ozone is made per kilowatt hour, while the ordinary method of preparing ozone by the silent discharge yields 15 grams ozone in 3-4 per cent solution, per kilowatt hour.

E. RENOUF.

An Investigation to Determine whether there is Change in Weight in Chemical Reaction.

The classical work of Landolt¹ on this problem is well known. Since his earlier results were published a number of investigations have been carried out along the same line. Landolt has now extended his earlier experiments, and the object of this note is to give a brief review of what he has done and what results he has obtained.

For the former work Landolt had at his disposal one of the finest chemical balances that had ever been constructed up to that time. It was capable of weighing 500 grams to within a few thousandths of a milligram, or at most a hundredth of a milligram.

The solutions of the two substances that were to be allowed to act upon one another were placed each in one arm of an inverted U-tube. Another U-tube of very nearly the same weight and external surface was used as a tare. After the first double weighing had been effected, the solutions were brought together by tilting very slowly the inverted U-tube. This was to prevent the reaction from proceeding rapidly and producing large changes in temperature in the containing vessel.

This earlier work of Landolt was a model of care and pre-

¹ Z. physik. Chem., 12, 1, 1903.

caution, and every conceivable source of error was taken into account. In this manner the following reactions were studied:

- I. $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$;
- II. $\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$;
- III. $2\text{I} + 2\text{Na}_2\text{SO}_3 = 2\text{NaI} + \text{Na}_2\text{S}_2\text{O}_6$;
- IV. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O} + \text{KOH} = \text{CHCl}_3 + \text{CHO}_2\text{K} + \text{H}_2\text{O}$;
- V. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O} + \text{water} = \text{solution}$.

In nearly all cases the changes in weight that were found were larger, and much larger than the sum total of the known experimental errors. In *nearly all cases there was a loss in weight*. This amounted to as much as 0.177 of a milligram, while the experimental error was from 0.01–0.02 of a milligram. In a very few experiments a gain in weight was found, but this was nearly always very small, being of the order of magnitude of the experimental error.

Of the various investigations carried out after this earlier work of Landolt, that of Heydweiller¹ deserves very special mention. His work, like that of Landolt, was a model of accuracy in every respect.

He studied the following six reactions:

- I. The action of iron on copper sulphate.
- II. Solution of copper sulphate in water.
- III. Mixing copper sulphate with dilute sulphuric acid.
- IV. Mixing of copper sulphate with potassium hydroxide.
- V. Action of acetic acid on ammonia.
- VI. Action of sulphuric acid on barium chloride.

Heydweiller found changes in weight of the same order of magnitude as those found earlier by Landolt, and an important point is that, with the exception of two experiments, the change in weight was always negative—there was a *loss in weight during the reaction*.

Landolt, being provided with a new and improved balance, took up the problem again in 1901, and the results of this last work have just been published.² In these new experiments greater precautions, if possible, are taken than in the earlier investigation. It would lead too far to discuss these in any detail. The effect of change in temperature on the balance, and on the vessels containing the solutions, the position of the vessels on the arms of the balance, the effect of warming the vessels by the heat liberated during the reactions, the deposi-

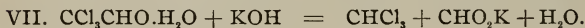
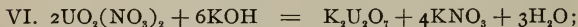
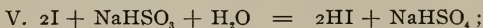
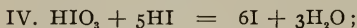
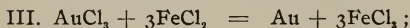
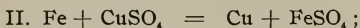
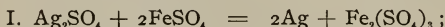
¹ Ann. d. Phys. (Drude), 5, 394 (1901).

² Sitz. d. kön. preuss. Akad. d. Wiss., Feb. 15, 1906.

tion of moisture on the surface of the vessels, the change in the volume of the solutions effected by the reactions, are some of the matters that were taken into account.

To determine the maximum experimental errors that were possible, experiments were carried out by introducing into the vessels substances that would not react chemically with one another. The errors were found to be, at most, of the order of magnitude from 0.01-0.02 of a milligram.

The reactions which Landolt has studied in this later work are the following :



VIII. Electrolysis of cadmium iodide.

To give an idea of the character of the results obtained by Landolt, his figures in the case of one reaction—the first—are given :

Observed changes in weight. Milligram.	Error in weighing. Milligram.
—0.085	0.009
—0.103	0.009
—0.068	0.010
—0.042	0.009
—0.029	0.009
—0.199	0.030
—0.137	0.028
—0.079	0.013
+0.003	0.004
—0.003	0.009

In some of the reactions the changes in weight found experimentally were scarcely larger than the experimental errors.

However, wherever appreciable changes in weight were found, they were always negative. That is, *whenever there was a change in weight, there was always loss in weight*, and the amount of the loss was of the order of magnitude indicated by the above results.

A relation of this kind is obviously of very great importance.

It raises the question as to whether the law of the conservation of matter holds rigidly when chemical reactions take place. The evidence for the existence of such a law is based, primarily, upon weight remaining unchanged when chemical reaction occurs, and in the determination of this factor we are, obviously, bound by the limit of error of our experimental work. It seems, from this most refined investigation, that there is frequently slight loss in weight when chemical reactions take place.

Landolt attempts to account for this loss in weight, as we might imagine, in terms of the electron theory. He suggests that during chemical reaction the atoms are probably subjected to violent agitation, and it is quite conceivable that some electrons might be set free from the atoms and escape. These might easily pass through the walls of the containing vessels, thus reducing the mass of the reacting substances.

If this is the true explanation of the loss in weight in chemical reaction, then, as Landolt suggests, we should expect to obtain different losses in weight when the containing vessel had thick walls than when the walls were thin. Further, the loss would be different when different substances were used for constructing the vessels. These conditions remain for investigation in the future.

In terms of the electron theory of J. J. Thomson, it is quite conceivable that some electrons would be shot off during chemical reactions, and that the law of the conservation of mass, as usually understood, does not hold rigidly when substances are allowed to react with one another chemically.

This raises the further question, are any of our so-called laws of nature really rigid generalizations? We know that very few of them are, the number gradually decreasing as experimental work becomes more and more refined. It would scarcely be surprising to find that the best of them are only close approximations.

H. C. J.

REVIEWS.

ADOLF VON BAEYER'S GESAMMELTE WERKE. Herausgeben zur Feier des siebenzigsten Geburtstages des Autors von seinen Schülern und Freunden. Braunschweig: Fr. Vieweg und Sohn. 1905. Band I., pp. cxxxii + 990; Band II., pp. 1196. Price, M. 16.

The collected works of Nencki were reviewed some little time ago,¹ now we have those of Baeyer, issued by a committee in celebration of his seventieth birthday and edited by Dr.

¹ THIS JOURNAL, 34, 352 (1905).

V. Villiger. It is to be hoped that this indicates a growing fashion, as the custom of issuing the collected works of the leaders of science during their lifetime is entirely admirable. One of the most valuable features of the present book is a brief autobiography, which it is difficult to praise too highly. It is most fascinating reading, giving, as it does, a clear, simple and thoroughly modest account of the writer's struggles, difficulties and successes; moreover, his mention of other great men with whom he came in contact is natural and unforced, it is never disparaging, he always gives praise where it is due but, on the other hand, there is entire freedom from that conventional eulogy which is as common as it is wearisome.

Johann Friedrich Wilhelm Adolf Baeyer was born October 31, 1835, in Berlin. Hitzig, his maternal grandfather, in addition to his position in the criminal judicature, stood high in the literary circles of Berlin on account of his biographical writings; his uncle, Franz Kugler, was the art historian, and his father was in the General Staff, at that time captain, later rising to the rank of lieutenant-general. When a small boy, Adolf Baeyer passed his holidays with his father, who was engaged in geodetic surveys, and spent days amusing himself with such flowers or animals as he could find, thus becoming accustomed to original, close observation. A better training for any child could hardly be conceived. Baeyer entered chemistry by the firework route and, to avoid worse things, on his ninth birthday his father gave him a copy of Stöckhardt's "*Schule der Chemie*." With his pocket money of $12\frac{1}{2}$ cents weekly, he fitted a room as a laboratory, worked through all the experiments and gave lectures to a boy friend, who, in return, cleaned the apparatus. It is interesting to remember that Ostwald has recently stated that he was also first attracted to chemistry by the study of Stöckhardt's book; such a record is probably unique. Baeyer's earliest original discovery was made at this time; he prepared the compound $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$, from copper sulphate and sodium carbonate. E. Mitscherlich, who was visiting at the house, was shown the crystals and stated that they were novel, but Baeyer had no analytical balance and no knowledge of how to publish new observations; four years later the compound was described by Struve.

During his thirteenth year Baeyer left the Friedrich Wilhelm Gymnasium and entered Schellbach's School of Natural Science and Mathematics. Here his interest in chemistry received a powerful stimulus, especially in connection with uric acid and indigo, but he was also much attracted to mathe-

matics and physics ; however, by the time he was 15 years of age botany had supplanted all three of these subjects in his esteem.

At the University of Berlin Baeyer thoroughly enjoyed himself, in company with von Richthofen, Weingarten, Paalzow, Ernst Haeckel and Paul Ascherson; he studied physics under Magnus and, although not prone to attend lectures, he made an exception in the case of those of Dirichlet on mathematics. After his one year military service, Baeyer was weary, nothing interested him but chemistry, so he decided to become a chemist and went to Bunsen, at Heidelberg, in 1856. Evidently his previous work had been good, for after a summer semester at analysis, he was started on a research on the reaction of bromine and tartaric acid, a part of the photochemical work of Bunsen and Roscoe ; Baeyer says of this that the work was purely mechanical and the ideas which he expressed in the published paper were Bunsen's. Later, the assistant Pabal, who had been requested by Bunsen to investigate the various methyl chlorides, transferred the subject to Baeyer. One method of preparing methyl chloride was by heating cacodylic acid with hydrochloric acid. Consequently, at the end of the research, Baeyer was possessed of a considerable quantity of cacodylic acid. On showing it to the assistant Schischkoff and asking what he had better do with it he received the reply, "at present it is the fashion to treat everything with phosphorus pentachloride." This advice was followed with results that are well known. Evidently, too, "fashion" in chemistry is not so new as some users of the Grignard reaction might imagine.

In Bunsen's laboratory Baeyer learnt analysis and gasometric methods, but nothing else, for by that time Bunsen had entirely lost his interest in organic chemistry, consequently, in the spring of 1857, Baeyer went to Kekulé, who was then privatdocent at Heidelberg ; it was here that cacodyl trichloride was prepared. Kekulé's laboratory consisted of a single room, without draught other than was afforded by the defective flue of a neighboring kitchen, the result was that one day he found Baeyer semi-delirious, with a greatly swollen face, due to the accidental inhalation of methylchlorarsine—surely a rather strenuous method of discovering a new compound and investigating its properties ! Baeyer returned to Berlin at Easter, 1850, to obtain the Ph.D. degree ; his dissertation included the results of his work on arsines and, as it had been conceived and executed entirely alone, he obviously deserved far more credit than the majority of candidates. The work was, how-

ever, not understood by Mitscherlich, H. Rose and Magnus, and although their attitude to him personally was paternal, as a candidate his reception was chilly. Eventually he received a second mark. It is instructive to compare this result and the quantity of research which Baeyer had done with present-day methods of producing Ph.Ds.

The winter of 1858-9 was spent with Kekulé at Ghent, work being commenced on uric acid derivatives. His efforts to prepare uric acid by the elimination of water from pseudouric acid failed, owing to the use of too concentrated mineral acid, as was shown, later, by E. Fischer.

The spring of 1860 saw Baeyer as "privatdocent," but without any laboratory and without the private means for fitting one. In the autumn, however, he became instructor of organic chemistry at the "Gewerbe-Institut," now the "Technischen Hochschule." The appointment was by no means an attractive one, it was terminable at 3 months' notice and the salary was M. 1800, say \$450 per annum, of which half had to be turned over to assistants, but a good laboratory was provided and the next 3 years were spent on the uric acid researches, in conjunction with Damm, Deichsel, Herzog and Heintzel. After the death of E. Mitscherlich, in 1863, and of H. Rose, in 1863, and pending the arrival in Berlin of A. W. Hofmann, in 1865, the lectures were given by several junior members of the University; Baeyer also secured the necessary permission to give a course and made the needful preparations, but not a single student attended!

In 1865 Baeyer was to have succeeded Kolbe in Marburg, but, over the head of his minister, the reigning sovereign appointed Carius. The following year, with Hofmann's support, Baeyer was made honorary "Extraordinarius," and in 1870 he received a call to Königsberg, as successor to Werther. This was declined because the laboratory was represented as being unhealthy, but, on the ground of having received the call, of having served faithfully for 10 years, and of the research work which had been done in his laboratory, he applied to the authorities for his appointment to be made permanent and for a small increase in salary, both requests received a brusque refusal. The discovery of artificial alizarin had been made in Baeyer's laboratory two years previously. In 1868 occurred his marriage with a daughter of Geheimrat Bendorff.

In 1872 it was proposed to appoint Baeyer as professor of pure chemistry in the medical faculty of the University of Berlin, the idea being to have one place in Germany where

medical students could obtain advanced instruction in chemistry. Naturally the faculty objected, because it was impossible for them to believe that any one who had not studied anatomy could possibly teach chemistry—to medical students. The same notion is still widely prevalent in this and other countries, in spite of the work of E. Fischer, a pure chemist, which has done more for physiological chemistry than that of any other single man. The proposal was, however, abandoned on account of the resignation of the minister of education. Among other students in Baeyer's laboratory at this time may be mentioned Liebermann, C. Graebe and Victor Meyer. In 1872 Baeyer was called to Strassburg and in the spring of 1875 he succeeded Liebig in Munich. The latter had stipulated, when he went there, that he should have no practical classes, hence Baeyer had to build and equip a laboratory, which was an advantage in so far as he was saved from taking over a quantity of useless material, of students and assistants. The inorganic work was given to Volhard, who was the only legacy from Liebig, and his methods of instruction have never been improved upon by his successors. The magnitude of this statement will be apparent when it is mentioned that his place was occupied, in turn, by E. Fischer, Clemens Zimmermann, v. Pechmann and G. Krüss; the methods are also in use in other German laboratories and in that of the Johns Hopkins University.

Baeyer concludes his recollections by some remarks on chemical education, the training of technological chemists and the evils of examinations. These last might well be taken to heart by the English authorities, whose practice is exactly the opposite to that advocated by Baeyer; the results to English chemistry are notorious. As regards the second subject, it may be said that the first and last essential is that the would-be technologist should be taught chemistry—in the broadest possible way. This has been accepted in Germany, its truth is beginning to be realized by "Captains of Industry" here, but in England they are, apparently, still as far as ever from recognizing it.

The description, by E. Fischer, of the life at Strassburg is, needless to say, delightful, witty and full of good stories. Unfortunately, space is lacking to reproduce them all. E. and O. Fischer had started on a tour from Bonn, thoroughly dissatisfied with the instruction in analysis which they had been receiving there, indeed, E. Fischer had almost decided to abandon chemistry in favor of physics. They came to Strassburg and met the "Inspector" (a kind of glorified janitor),

who proved to be most affable. Now they argued 'if the Inspector, who is well known to be *the* most important person in an institution, is agreeable to such a degree, to what dizzy height in this respect must not the assistants, and particularly the professor attain?' Therefore they remained. Bunsen's methods of analysis were taught by F. Rose, who had accompanied Baeyer from Berlin, and Fischer describes the fascination which quantitative analysis has had for him ever since. In those days it was not customary to make organic preparations, practical organic chemistry was learned by working with the substances to be used in the graduation work. Fischer, for example, began his research without having made a combustion or knowing how to distil ether. These and other matters the student acquired partly by the light of nature, often by the direction of a more senior student and, occasionally, from an instructor. Fischer was started on an investigation of hydromellitic acid; shaking machines had not been invented and he was walking about the laboratory, which was a temporary structure, with a bottle containing 0.5 kilo of mellitic acid and 25 kilos of mercury, his foot went through the floor board, with the result that half the mercury and the whole of the acid were lost, this, he says, 'suggested to Professor Baeyer the desirability of giving him another subject on which to work'. One would like to record the names of the students, instructors and professors who were then at Stassburg and relate some of their adventures, including that of Meer, who, because of his work on chlorphenol, was turned out of his dwelling and refused admission to any restaurant or boarding-house, fortunately for him, Mrs. Baeyer came to the rescue.

The discovery of phenylhydrazine is too good to be omitted. A student had been told to make diphenol from benzidine; he obtained only a tar. Doubtless, as is usual with students, he explained that he had done everything thinkable and that the result was due to the inherent perverseness of the material; doubtless, also, as is usual with organic instructors in such circumstances, Fischer did not attach any particular weight to his statements. At all events Fischer did the experiment himself and got a similar result! On consideration he decided that this was due to the oxidizing action of the nitrous acid, so he repeated the experiment in the presence of sodium sulphite and obtained crystals which were new to him and also to Baeyer. The substitution of aniline for benzidine gave him phenylhydrazine.

Following the autobiography, Baeyer gives an account of the leading ideas which have guided his researches; to compress it

would be an impertinence, it will suffice to say that it is of absorbing interest and should be read by every chemist. Such glimpses into the working of the mind of a great leader are invaluable. Baeyer's lecture on the synthesis of indigo, which was delivered on the occasion of the opening of the "Hofmann-Haus" in 1900, is also reproduced, then follows a list of all papers published from his laboratory. Although many of these do not bear his name, it is safe to say that all of them are indebted to him for criticism, advice, suggestion, or direct inspiration. This list occupies 63 pages.

The remainder of the volumes consists of Baeyer's own papers, which are grouped according to subject, into 19 sections, as follows: Organic arsenic derivatives, pp. 54; uric acid derivatives, pp. 124; indigo, pp. 184; researches connected with indigo, pp. 70; pyrrol and pyridine bases, pp. 38; dehydration and condensation, pp. 120; phthaleins, pp. 220; the hydroaromatic compounds, degradation of mellitic acid and the constitution of benzene, pp. 488; researches on terpenes, pp. 270; nitroso-derivatives, pp. 60; furfuraldehyde, pp. 22; acetylene derivatives and the strain theory, pp. 48; peroxides, pp. 100; the basic properties of oxygen, pp. 38; dibenzalacetone and triphenylmethane, pp. 168; miscellaneous papers on aromatic compounds, pp. 90; miscellaneous papers on aliphatic compounds, pp. 38; nomenclature, pp. 10; sundry papers, pp. 17. The photogravure portrait of Baeyer, at the beginning of Volume I., is an excellent likeness and adds greatly to the value of the books.

Of the many reflections which these volumes suggest, two appear to call for special mention. Contrary to what one might have anticipated, Baeyer owed nothing of his success to family influence, indeed, as we have seen, he had to struggle against many difficulties, and suffer from lack of appreciation.

Like A. W. Hofmann, Bunsen, Würtz and other great leaders, Baeyer had laid the foundations of his fame at an age when many men are only just beginning to think of commencing graduate work.

Of his papers it will suffice to say that, for years past, a considerable number of them have ranked among the chemical classics. Their clear, lucid style, the simplicity and directness of statement, and the records which they contain of the wonderful technique and experimental skill of their author alike testify to the master mind and hand.

All true chemists will join with the reviewer in offering their most respectful congratulations to Professor Baeyer on this happy method of celebrating his birthday, and in expressing

their sincere desire that he may long be enabled to continue his contributions to the further advancement of the science he loves so well.

J. BISHOP TINGLE.

DIE TIERISCHEN GIFTÉ. By EDWIN S. FAUST. Braunschweig: Friedrich Vieweg und Sohn. 1906. Price, M. 6.

The progress of knowledge in regard to the animal poisons is well illustrated by the inclusion of Dr. Faust's monograph in the series of "*Die Wissenschaft*" which, hitherto, has been devoted to monographs in the physical and chemical sciences. This distinction is entirely justified by a more exact knowledge of the animal poisons which has come, on the one hand, from their biological study, and on the other, from the application to them of those physiological-chemical methods which the last decade has seen so greatly defined. It is interesting to consider the very important part which the study by medical biologists of the phenomena of immunity has taken in advancing our knowledge of the chemistry of this class of poisons. Since the discovery of the peculiar reactions of the animal body which are now included generally under the term of "immunization," a valuable method has been discovered for establishing with accuracy identity or dissimilarity in many animal poisons. Even in cases in which the physiological reactions of the body to the poisons are not sufficiently distinctive to decide the question of relationship, the production of immunity in animals is often capable of deciding the doubtful results. It has been found that many of the animal poisons, belonging to a class of substances which chemically are difficult to define, produce, upon successive inoculation into animals, their antibodies. The latter are neutralizing in nature and are specific for the type of poison for which they have been developed. Thus, should animals be immunized with several kinds of snake venom, or poisonous blood sera, the resulting immune sera would be neutralizing for those poisons in venom or in serum with which the original poisons were in constitutional accord. By this means it has been possible to define chemically, with a considerable degree of accuracy, a number of animal poisons of which physiological studies alone had not entirely shown the relationship.

The complexity of many of the animal poisons, as brought out by this study, is often very great. To continue with venom as an illustration, it has been ascertained that of two venoms which produce similar effects on injection into animals, the effective poisons—say the blood-dissolving or hæmolytic and the nerve-destroying or neurotoxic poison—possess different chemical constitutions. We know nothing definite of the

ultimate chemical structure of these bodies, but by this "biological" reaction we can say, with confidence, that in spite of similarity of physiological effects a difference in chemical constitution exists. This knowledge, which must ultimately be of value to the organic chemist, may be somewhat disappointing to the medical investigator. Now that efforts are being made successfully to produce active antisera for vegetable and animal poisons which act injuriously upon and threaten the life of the higher animals, it adds greatly to the difficulties of the subject to be confronted with this tantalizing dissimilarity in the constitution of poisons, the physiological action of which is so much in accord. On the other hand, the value of the biological means of differentiation is enhanced by the very delicacy of the differences which it establishes.

Thus far chemistry, as such, has not succeeded in separating the animal poisons into their definite component parts and since these poisons have not, with very few exceptions, been obtained in states of purity, we are ignorant of their real nature. Even the term *toxalbumin*, which has been widely employed to designate them, is, in spite of its lack of definiteness, becoming more and more inapplicable as greater refinement of method removes from the poisons those obvious reactions upon which a belief in the albuminous nature of bodies has hitherto rested.

It will be impracticable in this review to do more than to indicate the subjects which are treated of in the present interesting compilation. After a general introductory chapter the poisons yielded by the class of vertebrata are discussed. Among the poisons which are considered are adrenalin, the poisonous crystalline principle of the suprarenal glands and the bile salts, all of which possess a high degree of toxicity. The larger part of the chapter, however, is devoted to the poisons yielded by snakes, the gila monster, the amphibia and fishes. More than half the book is devoted to this chapter. The remainder of the space is occupied with a description of the poisons yielded by the invertebrata—mollusks, arthropods, myriopods, insects, crustacea, worms, echinoderms and coelenterates. The literature has been carefully studied and a sufficient bibliography of the different subjects given. The treatment of the book is liberal and modern, and the author has indicated a grasp of the chemical and biological portions of his subject which shows a mastery of both.

S. FLEXNER.

A HANDBOOK FOR CANE SUGAR MANUFACTURERS AND THEIR CHEMISTS. By GUILFORD L. SPENCER, D.Sc. New York: John Wiley and Sons. 1906. pp. vi + 203. Price, \$3.00.

The fact that this valuable handbook has passed to its fourth

edition shows the avidity with which it has been received by the technical sugar world. At the time the first edition was prepared there was grave question whether a book of its nature would find any remunerative sale. In the whole cane sugar producing world there were probably not a dozen factories employing chemists. When the book was published, however, it stimulated the desire among manufacturers of sugar cane to secure the chemical control therein described, and at the present time there is a markedly changed condition of affairs. There is scarcely a manufacturer of sugar, from the sugar cane, whose business is of any magnitude, who does not employ a chemist.

In addition to the chemists, who are directly interested, the book is useful to all who are concerned in chemical technology. It is a type of admirable treatment of a chemico-technical subject, both in character and in the arrangement of its contents. While the book is devoted principally to the description of chemical methods and chemical control, it is sufficiently explicit in its purely technical chapters to be of interest and value to the engineer. The apparatus and the manipulation thereof are described in detail, and this is followed by an account of chemical methods of research and the best means to employ for the most efficient control of a sugar house. Tables which are constantly used both by the engineer and the sugar chemist are appended to the body of the work, the whole forming a compact volume of convenient size.

H. W. WILEY.

AMERICAN CHEMICAL JOURNAL

A METHOD OF DETERMINING HYDROGEN PEROXIDE: AND FERROUS SALTS AND OTHER REDUCING AGENTS.

BY W. E. MATHEWSON AND J. W. CALVIN.

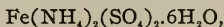
The fact that soluble titanium compounds give a deep yellow compound with hydrogen peroxide forms the basis of well known qualitative tests for both substances.¹ Weller's colorimetric method² for the estimation of titanium also depends on this reaction. The intensely yellow substance formed, usually considered to be titanium trioxide or the acid derived from it, is instantly decomposed by reducing agents and it would, therefore, seem that such compounds might be determined by titrating with standard solution of hydrogen peroxide, using a titanium salt as indicator. It was thought by the writers that if standard peroxide could be used in this way the process might be applied very advantageously in certain determinations. The peroxide is very reactive and is not only capable of acting as a strong oxidizing agent with most reducing substances, but can also reduce many of the stronger oxidizing

¹ Schön: Z. anal. Chem., **9**, 41, 330.

² *Ibid.*, **23**, 410, from Ber. d. chem. Ges., **15**, 2592.

agents and the method might be equally applicable to some reactions of the latter class. In this paper are given the results obtained with ferrous ammonium sulphate and sodium nitrite. These substances were chosen as they are well known reducing agents and seemed suitable for testing the method.

Ferrous Ammonium Sulphate.—A standard, approximately 0.1 N solution of ferrous ammonium sulphate, containing some excess of ammonium sulphate was prepared, several portions of different amounts measured from a burette, about 5 cc. of phosphoric acid added, to render the solution colorless, and sufficient water to make about 50 cc. About 5 cc. of a solution of titanium potassium sulphate was then poured in and the mixture titrated at once against peroxide. The titanium solution was made by fusing the dioxide with about 10 times its weight of potassium hydrogen sulphate, dissolving the fused material in cold, dilute sulphuric acid and filtering. The results obtained from these titrations being quite concordant, 4 portions of crystallized ferrous ammonium sulphate,



were weighed out, dissolved and titrated in the same way. The weights of the salt taken were 0.1985, 0.4480, 0.3405 and 0.4641 gram, respectively ; the number of cc. of peroxide taken were 5.73, 12.44, 9.86 and 13.16. The amounts of hydrogen peroxide required for 1 gram of the iron salt were found, therefore, to be 28.86, 27.77, 28.96 and 28.36 cc. As ammonium sulphate is stated to make the reaction between permanganate and oxalic acid take place more smoothly and much more rapidly, it was thought that possibly the much greater irregularities observed in these results than in those with the standard solution were due to the presence of excess of ammonium sulphate in the latter. Seven portions of the Mohr's salt were again weighed out, about an equal amount of solid ammonium sulphate added, and the remainder of the operation carried out as before, except that the solution of hydrogen peroxide used was somewhat more concentrated, about 0.15 N. The following are the data obtained ;

No.	Salt taken. Grams.	Peroxide required. cc.	Cc. of peroxide required per gram of salt.
1	0.1902	3.09	16.24
2	0.3420	5.54	16.19
3	0.4918	7.90	16.07
4	0.5374	8.74	16.26
5	0.6258	10.11	16.15
6	1.1133	17.82	16.01
7	1.4645	23.45	16.01

These results indicate that ferrous iron can be accurately estimated with standard hydrogen peroxide if the titre of the latter be fixed with a known amount of the same substance.

Three weighed portions of the salt were titrated against a peroxide solution and from the mean the normality of the latter was calculated. The normality was also determined by titrating against a carefully standardized permanganate solution. As the effect of slight overstepping of the end point necessary to give the liquid a tinge of color is to make the normality appear too high in the permanganate-peroxide solution, but too low in that of the iron against the peroxide, considerable care was taken to minimize this error. The titrations were made carefully and the reaction considered complete when the solution showed just a sufficient tinge of color to be recognized with certainty. The following are the data :

Titration of Peroxide against Ferrous Ammonium Sulphate.

No.	Salt taken. Gram.	Peroxide required. cc.	Cc. of peroxide required per gram of salt.
1	0.6771	11.54	17.04
2	0.5631	9.66	17.15
3	0.9563	16.23	17.02

Normality of H_2O_2 solution = 0.1498.

Titration of Peroxide against Permanganate.

10 cc. H_2O_2 solution = 13.37 cc. KMnO_4 solution.

25 cc. H_2O_2 solution = 33.35 cc. KMnO_4 solution.

Normality of H_2O_2 solution = 0.1507.

The agreement is satisfactory considering the strengths of

the solutions and the quantities used. As the hydrogen peroxide solution had been prepared by diluting the ordinary pharmaceutical preparation, the slightly higher value obtained with the permanganate may have been due to the presence of traces of foreign matter. As C. E. Smith has shown,¹ commercial hydrogen peroxide sometimes yields too high results when titrated against potassium permanganate because of the presence of organic substances. Small amounts of these would probably be without influence on the results obtained with ferrous sulphate.

The above indicates a simple method for determining the strength of samples of hydrogen peroxide. The solution is diluted with a known amount of water, so that its strength is reduced to about 0.2 N (0.3 per cent). About 2 grams of ferrous ammonium sulphate are weighed out, dissolved in a little water, and a few grams of ammonium sulphate and some phosphoric acid added. Some of the titanium solution is then poured in and the mixture titrated against the peroxide, the latter being added from a burette.

Sodium Nitrite.—In these experiments solutions of sodium nitrite of about 0.5 N or 0.2 N were used. As by the action of the acid present in the indicator there is a slight loss of nitrous acid when it is first added to the solution, a rough, preliminary titration was made to determine the approximate amount of hydrogen peroxide required, then, in the subsequent titration, almost this amount was added, the indicator poured in and the titration finished. The results obtained, while reasonably concordant, have been uniformly slightly too high. This is probably due, to some extent at least, to the fact that the reaction is quite slow near the end point. Probably reasonably accurate results can be obtained only when the titre of the peroxide is fixed with a known amount of nitrite.

Work is being continued in this laboratory with a view to testing the application of the above method to the estimation of certain organic compounds, readily oxidized by hydrogen peroxide in acid or in alkaline solutions.

¹ Chem. News, 80, 204.

Grateful acknowledgement is hereby made Prof. J. T. Willard, through whose kindness these tests have been made.

KANSAS STATE AGRICULTURAL COLLEGE.

ON A NEW METHOD FOR THE PREPARATION OF STANDARD SOLUTIONS.

BY S. F. ACREE AND R. F. BRUNEL.

The first difficulty that faces the individual beginning a series of exact volumetric analyses in acidimetry and alkalimetry is the preparation of an accurate standard solution of an acid or alkali. Among the acids used for making normal solutions by dissolving weighed amounts in the necessary quantity of water or other solvent, are potassium tetroxalate, oxalic acid and succinic acid. The chief objection to these is that they are weak acids and cannot be titrated with an error of less than 0.10 per cent. The second objection is that the first two substances cannot be made with a constant amount of water of crystallization, while if they are prepared in the anhydrous condition they do not long remain so. In solutions made from these substances by students the error may easily be 0.10-0.20 per cent.

Solutions of sulphuric and hydrochloric acids can be standardized fairly accurately by students by the barium sulphate and silver chloride methods, but this involves considerable time and care, and the barium sulphate method, especially, has several objectionable features.

In physical-chemical investigations the writers use standard solutions of hydrochloric acid and alkalies in conductivity water, which must be correct to 0.05 per cent. The standard hydrochloric acid solution is made very quickly and accurately as follows: A clean liter flask is nearly filled with conductivity water having the room temperature, and is closed with a one-hole rubber stopper through which passes a glass tube drawn out in a long capillary, reaching nearly to the bottom of the vessel.

The flask is weighed to within 0.001 gram, with a similar

liter flask filled with water on the other pan. Hydrochloric acid gas, generated from fused, pure ammonium chloride and concentrated sulphuric acid and passed through two Wetzell wash-bottles containing sulphuric acid, is run into the flask until the increase in weight is a little more than a gram-molecular weight. Before the final weighing is taken the solution must be at room temperature. Very little manipulation is required to run the exact amount of hydrochloric acid desired into the flask, but even if considerably more is obtained, the solution can be made up to the required volume by filling the flask up to the liter mark and adding the required extra volume from a burette. The contraction due to mixing 12 cc. of water with a liter of normal hydrochloric acid solution is only about 0.0001 cc., or practically nothing. The method adapts itself to the preparation of any smaller volume of solution of any desired strength.

Julius Thomsen¹ tried to determine the atomic weights of hydrogen and oxygen by weighing the quantities of hydrochloric acid gas and ammonia necessary to neutralize each other. His results did not agree with those of other investigators. The reason is now apparent, as several errors were present in his work which could have been excluded.

The first source of error is that due to the absorption of moisture from the atmosphere by the calcium chloride tubes used on the flasks in which the gases were collected and weighed. This error may be quite large and it is far better not to employ such drying tubes.

The second error is that due to his method of drying the hydrochloric acid gas. Thomsen dried the gas first with concentrated sulphuric acid, the very best method possible, and then *moistened* the gas by passing it over calcium chloride or magnesium chloride. These chlorides contain considerable water of crystallization and oxides which would react with the hydrochloric acid and form water. As a result, the hydrochloric acid gas contained some moisture, which made the real amount of hydrogen chloride used smaller than it was thought to be.

The third source of error was in the method of drying the

¹ Z. physik. Chem., 13, 398.

ammonia. Thomsen used potassium and sodium hydroxides in the stick form, in which considerable water is present. Fused potassium hydroxide, afterwards dried well over sulphuric acid, *in vacuo*, would have made this error very small. With these facts in view we shall repeat this work of Thomsen.

The normal solution made in the above way is accurate to within 0.01 per cent. The errors involved in weighing need not be more than 0.002 gram, and the moisture contained in the hydrochloric acid gas is not over 0.00005 gram, judging from the work of Dibbits.¹ Such a solution gives no precipitate with barium chloride, is practically free from carbon dioxide, silicates and all other impurities which are present in the best hydrochloric acid sold in the market. This fact is of the very highest importance to those using such standard solutions for very exact titrations or in physical-chemical investigations involving conductivity measurements. By this method a standard acid solution can be made very quickly, and its error is far smaller than that of the ordinary titration process; it can, therefore, be used directly for titration against alkalis without further standardization. The solution keeps a long time.

In the same way standard solutions of any dry gases, such as hydrogen bromide, hydrogen iodide, hydrogen sulphide, sulphur dioxide, ammonia, chlorine, etc., in any solvent, can be prepared. The writers use this method for making standard alcoholic hydrochloric acid solutions.

For determining the strength of solutions of pure hydrochloric and sulphuric acids the following plan is much better than the silver chloride and barium sulphate methods. Sodium bicarbonate was crystallized twice and was then free from chlorides, sulphates and silicates. Approximately 4.12 grams of this were put into a tall beaker, covered with a watch-glass having a hole in the center and titrated with the necessary volume, or weight of normal acid—about 50 cc. For very accurate titrations the carbon dioxide should be removed from the solution in a vacuum, the end point being obtained when the faintly pink solution remains unchanged in color after standing in a vacuum for some time. The solution is then

¹ Z. anal. Chem., 15, 121.

evaporated to dryness in a weighed platinum dish and heated to dull redness, until the sodium chloride is dry and the weight constant. A similar platinum dish is treated in the same way and used as a tare. From the weight of the sodium chloride or sodium sulphate and the volume or weight of the acid solution used, the strength of the latter can be easily determined. The total errors of this method should not be more than 0.05 per cent. The titration error should not be over 0.01 cc. in 50 cc., or 0.02 per cent, and the weighing error not more than 0.01 per cent. The method can be used for the determination of the strength of a solution of any acid whose sodium salt can be dried and weighed accurately. The titration error is larger with weaker acids.

In a similar manner the exact strength of a solution of pure sodium or potassium hydroxide can be determined by evaporating an exact amount, approximately 50 cc., with pure hydrochloric acid. The weight of the chloride obtained and the volume or weight of the alkali solution give the data necessary for determining the strength of the alkali solution. The unknown strengths of an acid solution and of an alkali solution can be determined simultaneously by neutralizing 50 cc. of the acid solution with the necessary amount of the alkali solution and evaporating the mixture to dryness, as above. The weight of the dry salt and the volumes of acid and alkali solutions taken furnish the necessary data. The solutions of acid and alkali must be free from appreciable quantities of silicates, chlorides, sulphates or other impurities.

Special experiments by Mr. G. H. Shadinger showed that methyl orange is much more sensitive to carbonic acid than is popularly supposed. When carbon dioxide, purified by being passed through two Geissler potash bulbs containing sodium bicarbonate solution, was run into a solution of 3 grams of sodium chloride, in 50 cc. of water containing a drop of 1 : 2000 solution of methyl orange, the pink color produced was discharged by 0.06–0.40 cc. of 0.1 N potassium hydroxide. Further experiments showed that these solutions, made pink by carbon dioxide, correspond in color to similar solutions made pink by 0.06–0.20 cc. of 0.1 N hydrochloric acid, the intensity of the

color varying with the degree of saturation of the solution with the carbon dioxide. When these solutions, saturated with the gas, are vigorously stirred and shaken, as in a titration experiment, the pink color corresponds to that produced by 0.06–0.10 cc. 0.1 N hydrochloric acid under the same conditions. Solutions made pink by carbon dioxide become brown very quickly in a vacuum, whereas similar solutions made pink by hydrochloric or sulphuric acid are not changed in color by such treatment. It is, then, very probable that analyses of carbonates by standard acids in the presence of methyl orange, as ordinarily made, are undertitrated, and the per cent of carbonate found is too low.

Standard Hydrochloric Acid Solutions.

By the method described above, a hydrochloric acid solution was made up to be 0.99987 N. The molecular weight of hydrochloric acid was taken to be 36.458. If the molecular weight 36.471, found by Dixon and Edgar,¹ which is a mean between the values found by Stas and by Richards and Wells,² were used, the acid would be 0.99953 N.

This solution was analyzed by the sodium bicarbonate method described above, but the carbon dioxide was not completely removed from the solutions. This error, however, was nearly compensated by the use of the value 23.05 for the atomic weight of sodium instead of 23.01, an error of 0.08 per cent of the weight of sodium chloride. The hydrochloric acid was measured from very carefully calibrated burettes. Three analyses are given in the following table:

Volume of HCl solution. cc.	Weight of NaCl. Grams.	Strength of HCl solution.
30.30	1.7730	1.0002 N
30.50	1.7833	0.99937 N
47.24	2.7629	0.99976 N

Average = 0.99972 N, or 0.015 per cent low.

These results show that solutions of hydrochloric acid, prepared as above, are as accurate as any ordinary analytical

¹ Chem. News, 91, 263.

² J. Am. Chem. Soc., 27, 459.

work requires. The writers believe that the sources of error noted above could be further reduced so that the method would serve for determining the ratio of the atomic weights of chlorine and sodium. For a number of years the value 23.05, obtained by Stas, has been generally accepted, but the recent very accurate work of Richards and Wells gives the value 23.01. If the total errors in the above method can be reduced to 0.02 per cent the writers believe it will furnish reliable evidence in favor of one or the other of the above values for sodium.

A further example of the accuracy and convenience of the sodium bicarbonate method for estimating the strength of acid solutions is given. A normal solution of sulphuric acid was made volumetrically through two other solutions, using about 15 cc. in the titrations. The titration error might then be about 0.20 per cent. This solution was analyzed by the barium sulphate method, the error being not more than 0.10 per cent; 20.68 cc. gave 2.4170 gram BaSO_4 , or the solution was 1.0013 N. It was then analyzed by the sodium bicarbonate method, under the conditions given above, with the following results:

Volume of H_2SO_4 solution. cc.	Weight of Na_2SO_4 . Grams.	Strength of H_2SO_4 solution.
47.32	3.3722	1.0026 N
45.33	3.2290	1.0022 N
Mean = 1.0024		

If this last value be considered accurate, the results found by the different methods check very satisfactorily. From the titrations the acid appeared to be exactly normal, but there was a possibility of 0.20 per cent error. The barium sulphate method, with a possible source of error of 0.10 per cent, gave a result 0.11 per cent below that obtained by the bicarbonate method.

Standard Ammonium Hydroxide Solutions.

An attempt was made to prepare standard ammonium hydroxide solutions by passing the dried gas into water in a weighed flask, under conditions similar to those employed in the preparation of standard hydrochloric acid. The concen-

trated commercial ammonia solution was treated with lime water to remove the carbonates ; it was then warmed gently in a flask and the gas was dried by passing it through towers containing quicklime and potassium hydroxide in sticks, and finally through a glass tube 6 feet in length, filled with broken potassium hydroxide, which had been fused and dried over concentrated sulphuric acid. The gas was then practically free from carbon dioxide and moisture,¹ and probably contained very little pyridine.

Several attempts to prepare solutions about 0.2–0.5 N showed that such solutions lose ammonia very quickly when exposed to the air, or when transferred to other vessels. That the method could be relied upon to give standard solutions was proved conclusively ; such solutions, however, will not remain long unchanged.

A solution was made by passing 1.2450 grams of ammonia into 250 cc. of water ($N = 14.04$, $H = 1.008$). This solution was then 0.29184 N. It was analyzed as follows : Normal hydrochloric acid solution, nearly sufficient to neutralize 50 cc. of the above ammonium hydroxide solution, was run into a beaker. The ammonium hydroxide solution was removed from the flask by means of a 50 cc. pipette containing a small layer of ligroin to prevent the escape of ammonia, and the solution was immediately allowed to run into the hydrochloric acid solution, the point of the pipette being immersed.

Two analyses showed 50 cc. of the ammonium hydroxide solution to be equivalent to 14.58 and 14.58 cc. of normal hydrochloric acid ; calculated, 14.59 cc. The strength of the ammonium hydroxide was 0.2916, or the error in the method was 0.07 per cent.

These standard solutions of hydrochloric acid and ammonium hydroxide are sufficiently accurate to warrant us in believing that the principle of using weighed quantities of well-dried gases for making up standard solutions is one worthy of further study, and this will be done in the near future.

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May 1, 1906.

¹ Van der Plaats : *Rec. Trav. Chim.*, 6, 45.

ON THE CONSTITUTION OF AMALGAMS.

[PRELIMINARY COMMUNICATION.]

BY GEORGE MCPHAIL SMITH.

As the result of investigations by Ramsay, Heycock and Neville, Tammann, and G. Meyer on dilute solutions of metals in other metals, it is generally accepted as a fact that, in solution, as a rule, the metals exist in the same state of aggregation as in the gaseous form; *i. e.*, that in solution the atom of a metal is identical with its molecule.¹

According to this prevailing view, it is tacitly assumed that the metals, as a rule, dissolve as such in other metals. This, however, is not necessarily the case and, just as among solid alloys we have the two classes, chemical compounds and mechanical mixtures to deal with, so it appears possible, if not probable, that liquid solutions of metals in metals may also comprise these two classes of substances.

It is the purpose of the present paper to discuss, from the above point of view, the results of Ramsay, Tammann and others; especially with reference to the constitution of the liquid alkali amalgams.

In 1879 Berthelot² published the heats of formation of potassium and sodium amalgams, and showed that, in these amalgams, the solution of the alkali metal in mercury considerably lowers the heat of oxidation of the former. Indeed, in the analogous amalgams, KHg_{12} and NaHg_6 , the heat of oxidation of potassium is less than that of sodium, the values for the two alkali metals in these amalgams being of an inverse order as compared with those for the metals themselves.

Berthelot found that the amalgam NaHg_6 , on being dissolved in 3 times its weight of mercury, absorbed -2.8 cal., and -2.9 cal. on being dissolved in 18 parts of mercury at 17° . These numbers agree well with one another, and they approach in value the heat of fusion (-3.36 cal.) of the mercury

¹ Kerp: *Z. anorg. Chem.*, **17**, 286f (1898). Schoeller: *Z. elek. Chem.*, **5**, 259 (1898). Erdmann: *Z. anorg. Chem.*, **32**, 404 (1902). Ostwald: "*Lehrbuch*" I., pp. 737, 767; II., i., pp. 859, 862 (1903).

² *Ann. Chim. Phys.*, [5], **18**, 433.

in the amalgam—a relation that is found to exist between the heat of solution of the highest hydrated salts and the heat of fusion of the water contained in them. From this and other data, Berthelot concluded that these amalgams were compounds analogous to hydrated salts.

More recently Kerp and Böttger,¹ Maey,² Guntz and Ferée,³ Kurnakoff,⁴ and Haber and Sack⁵ have investigated the amalgams of the alkalies and alkaline earths, and have established beyond a doubt the existence of definite compounds among them. Kerp and Böttger follow Berthelot in considering the crystalline alkali amalgams, such as NaHg_6 and KHg_{11} , as analogous to hydrated salts, *i. e.*, as being made up of a fundamental compound of mercury and alkali metal, combined with various amounts of mercury of crystallization.

Guntz and Ferée⁶ found that, when a solution of sodium in mercury is allowed to crystallize at -19° , crystals of NaHg_8 separate. These, on coming to the room temperature, break up into NaHg_6 and liquid amalgam. Similarly, Kerp and Böttger⁶ found that, on heating NaHg_6 , it breaks up into a crystalline amalgam richer in alkali and liquid amalgam.

The liquid amalgams, however, are regarded by Kerp and Böttger as being solutions of sodium or potassium in mercury, in the atomic state.⁷

Haber and Sack,⁸ on the other hand, clearly express their conviction that sodium does not dissolve in mercury in the monatomic condition. They say: "Als beweisend für dieselbe werden die Meyer'schen Messungen für Amalgam-Konzentrationsketten angesehen. Aber deren Ergebnis erlaubt keine Entscheidung darüber, ob das Natrium in Atomform oder in Gestalt der Verbindung Hg_5Na oder überhaupt Hg_nNa im Quecksilber sich befindet. Sie lehren nur, dass es

¹ Z. anorg. Chem., 17, 284 (1898); 25, 1 (1900).

² Z. physik. Chem., 29, 119 (1899).

³ Compt. rend., 131, 182 (1900).

⁴ Z. anorg. Chem., 23, 439 (1900).

⁵ Z. elek. Chem., 8, 245 (1902).

⁶ Loc. cit.

⁷ Loc. cit., 17, 286f.

⁸ Loc. cit., p. 255.

weder als Na_2 , noch in einer Verbindung Hg_nNa_2 darin auftreten kann. Ramsay's Autorität kann zu gunsten der Einatomigkeit des Natriums im Quecksilber keine Instanz abgeben, denn seine Dampfdruckerniedrigungen sind gerade bei diesem Metall anormal und er erörtert selbst die Möglichkeit, dass Legierungen auftreten. Sodann arbeitete Ramsay bei 270° ,¹ also bei einer Temperatur, wo Umwandlungen der Amalgame andere Zustände als bei Zimmertemperatur schaffen. Es muss, unseres Erachtens, als die best begründete Auffassung angesehen werden, dass die verdünnten Natriumamalgame bei gewöhnlicher Temperatur Lösungen von Hg_6Na und Hg_5Na in Quecksilber sind."

It will be shown, in the following, that Ramsay's results, as well as those of Heycock and Neville, and of Tammann, do not necessarily indicate the presence in solution of metals in the atomic state; they are just as well in harmony with the presence of compounds in solution. This, as is seen from the preceding quotation, completely escaped Haber's notice; even if Ramsay's results for sodium had been normal, they would not necessarily have indicated its presence in the atomic condition. That the same holds in the case of the measurements of G. Meyer has already been pointed out by Haber.²

In 1889, Ramsay³ determined the vapor pressures, at the boiling point of mercury, of a series of dilute solutions of metals in mercury. In every case he observed a lowering of the vapor pressure, due to the presence of the metal in solution. From his results he calculated the molecular weights of the dissolved metals, as shown in the following abbreviated table where s = the weight of metal dissolved in one gram-molecule, *i. e.*, in 200 grams of mercury; p = the pressure of mercury vapor in mm; $p-p_1$ = the observed depression in mm.

In his table, Ramsay used the per cent, P, of the dissolved metal in the solution, instead of the amount of metal dissolved in 100 grams of mercury. From P in his table, the values of

¹ Ramsay really worked at the boiling point of mercury.

² Z. physik. Chem., 41, 399 (1902).

³ J. Chem. Soc., 55, 521.

$\frac{1}{2}s$ have been calculated. The molecular weights found are practically the same in both cases.

Table I.

	Weight of metal in 100 grams of mer- cury. $\frac{1}{2}s$.	Atoms of metal per 100 atoms of mer- cury.	p .	$p-p_1$.	Molecular weight found. $\frac{sp}{p-p_1}$.	Atomic weight.
Lithium	0.05973	1.70	763.6	12.9	7.07	7.03
Sodium	0.21516	1.87	766.8	17.9	18.4	23.05
Potassium	1.0285	5.26	742.5	49.6	30.8	39.15
Barium	0.61445	0.90	762.0	12.3	76.1	137.4
Magnesium	0.58541	4.82	749.8	40.6	21.6	24.36
Zinc	1.0319	3.16	755.4	23.6	66.0	65.4
Cadmium	1.9596	3.51	740.0	27.4	105.8	112.4
Aluminum	0.39657	2.94	758.5	18.1	33.2	27.1
Gallium	0.79171	2.27	767.1	17.3	70.2	70.70
Thallium	1.6942	1.66	745.6	13.3	190.0	204.1
Tin	1.1552	1.94	754.1	14.7	118.5	119.0
Lead	2.0616	2.00	762.1	15.4	204.0	206.9
Antimony	1.5497	2.58	742.6	14.3	160.9	120.2
Bismuth	3.9198	3.77	762.1	26.8	222.9	208.5
Manganese	0.31318	1.14	755.0	8.5	55.6	55.0
Silver	1.7387	3.22	750.0	22.8	114.4	107.93
Gold	1.5651	1.59	760.4	11.3	211.6	197.2

On inspecting the table it will be seen that the molecular weights found for many of the metals are expressed by numbers very closely approximating to their atomic weights. For some of the metals, however, the numbers do not agree very well.

The molecular weight of a substance, in dilute solution, may be calculated from the formula

$$\text{Mol. wt.} = \frac{M \cdot \frac{1}{2}s \cdot p}{100(p-p_1)},$$

in which M is the molecular weight of the solvent, and the other letters have the same significance as in the preceding table. In this formula, the observed depression ($p-p_1$) depends only upon the number of molecules of the dissolved substance in a given quantity of the solvent, hence this depression would be practically the same, whether a given, very small

weight of lithium, for example, were dissolved in a given, relatively very much greater quantity of mercury, in the form of lithium atoms, or in the form of molecules of a compound, LiHg_n , containing only one atom of lithium to the molecule. That this actually is the case may be seen from the following table, which has been calculated from the preceding one, and in which only those metals have been included which are known to form compounds with mercury. In Table II. m = the weight of compound dissolved in 100 grams of mercury. It was obtained from $\frac{1}{2}s$ in the preceding table, according to the formula

$$m = \frac{\frac{\frac{1}{2}s \cdot \text{mol. wt. of MHg}_n}{\text{at. wt. of M}} \cdot 100}{100 - \left(\frac{\frac{1}{2}s \cdot \text{mol. wt. of MHg}_n}{\text{at. wt. of M}} - \frac{1}{2}s \right)}$$

Table II.

	m .	Molecules of com- pound per 100 atoms of mer- cury.	p .	$p-p_1$.	$\frac{2m \cdot p}{p-p_1}$.	Molecular weight.
LiHg	1.7896	1.73	763.6	12.9	211.8	207.03
LiHg_3	5.4490	1.79	763.6	12.9	645.1	607.03
LiHg_5	9.3515	1.86	763.6	12.9	1107.1	1007.03
NaHg_2	4.1021	1.94	766.8	17.9	351.4	423.05
NaHg_6	12.857	2.10	766.8	17.9	1101.5	1223.05
KHg_3	12.891	5.87	742.5	49.6	385.9	439.15
KHg_4	27.910	6.65	742.5	49.6	835.6	839.15
KHg_6	47.642	7.68	742.5	49.6	1426.4	1239.15
BaHg_{12}	12.711	1.00	762.0	12.3	1575.0	2537.4
MgHg	5.6639	5.05	749.8	40.6	209.2	224.36
MgHg_6	41.346	6.78	749.8	40.6	1527.2	1224.36
AgHg	5.1258	3.33	750.0	22.8	337.2	307.93

With regard to the existence of the compounds enumerated above, reference may be made, in addition to the papers already cited, to the work of Schüller¹ and Ogg². The compound MgHg_6 is described by Kerp and Böttger,³ but MgHg is not

¹ Z. anorg. Chem., 40, 385 (1904).

² Z. physik. Chem., 27, 285 (1898).

³ Loc. cit.

mentioned in the literature. Magnesium amalgams, however, have not been investigated to any extent.

On comparing the two tables, it will be seen that the values found for LiHg and AgHg in the second table agree with their theoretical molecular weights about as well as those found for Li and Ag in the first table agree with their atomic weights. Values found for compounds of sodium, potassium and barium with mercury agree better than those for the metals themselves; but the number found for MgHg_6 does not agree so well. For the compound MgHg , however, whose existence is not improbable, the values are in good agreement. The crystalline amalgams, NaHg_2 and KHg_2 , melt without decomposition at 346° and $269^\circ.7$, respectively. Solid sodium and potassium amalgams richer in mercury are decomposed by heat into free mercury and a crystalline amalgam richer in alkali metal, Cf. Kurnakoff¹ and Schüller.¹

On the other hand, Puschin,² in order to determine whether mercury forms compounds with zinc, cadmium, bismuth, lead and tin, has investigated the melting curves, the electromotive forces, and the microstructure of the amalgams of the metals in question. His results lead to the conclusion that the amalgams of these metals correspond to solid solutions or isomorphous mixtures, and that the assumption of the existence of definite chemical compounds in their case, as given by various authors,³ has no experimental foundation. Bijl⁴ had previously reached the same conclusion in regard to cadmium amalgam. Since the values found for these metals by Ramsay agree very well with their atomic weights, we are, perhaps, justified in concluding that they exist, when dissolved in mercury, in the atomic condition.

In a series of measurements, similar to those of Ramsay, Tammann⁵ made use of the cryoscopic method. He employed mercury as a solvent and obtained the results in Table III., where m = the weight of metal dissolved in 100 grams Hg; n =

¹ *Loc. cit.*

² *Z. anorg. Chem.*, **36**, 201 (1903).

³ Cf. Puschin: *Loc. cit.*

⁴ *Z. physik. Chem.*, **41**, 641 (1902).

⁵ *Ibid.*, **3**, 441 (1889).

atoms of metal per 100 atoms of mercury ; $t-t_1$ = the depression of the freezing point of mercury.

Table III.

	<i>m.</i>	<i>n.</i>	$t-t_1$.	Molecular weight found. $\frac{425 \cdot m}{t-t_1}$.	Atomic weight.
Potassium	0.018	0.092	0.27	28.4	39.15
"	0.030	0.147	0.42	30.4	"
"	0.091	0.448	0.73	53.0	"
"	0.112	0.552	1.04	45.8	"
"	0.137	0.676	1.24	46.9	"
Sodium	0.022	0.191	0.39	24.0	23.05
"	0.043	0.374	0.72	25.4	"
"	0.112	0.974	2.23	21.3	"

On the assumption that the compounds KHg_{12} and NaHg_6 ¹ were present in Tammann's solutions, the following table has been calculated :

Table IV.

	<i>m.</i>	<i>n.</i>	$t-t_1$.	$\frac{425 \times m}{t-t_1}$.	Molecular weight.
KHg_{12}	1.1340	0.093	0.27	1785	2439.15
"	1.9041	0.156	0.42	1927	"
"	6.0046	0.492	0.73	3496	"
"	7.4923	0.614	1.04	3062	"
"	9.3182	0.764	1.24	3194	"
NaHg_6	1.1809	0.192	0.39	1287	1223.05
"	2.3339	0.379	0.72	1377	"
"	6.3109	1.026	2.23	1203	"

Tammann says his measurements are only of an orientating character ; they do vary greatly among themselves. The mean found for potassium is 40.9 instead of 39.15, and for sodium it is 23.57 instead of 23.05. The above table gives for KHg_{12} a mean of 2693 instead of 2439.15, and for NaHg_6 1289 instead of 1223.05. These values agree within the error of experiment.

In two series of cryoscopic measurements, much more elaborate than those of Tammann, Heycock and Neville² used as solvents sodium and tin. Their results, for the first series,

¹ Cf. Kerp and Böttger : *Loc. cit.* 25, 1.

² J. Chem. Soc., 55, 666 (1889) ; 57, 376 (1890).

are given in a modified form in the following table. Heycock and Neville expressed their results in terms of the atomic fall, *i. e.*, the fall produced in the freezing point of the pure solvent by dissolving one atomic weight of metal in 100 atomic weights of sodium. Numerous experiments were performed in the case of each dissolved metal and, in the preparation of the above table, the experiment under each metal has been selected in which the mean atomic fall found in that series was most nearly approximated. In Heycock and Neville's tables this was for gold (6), for thallium (6), for mercury (5), for cadmium (7), for potassium (3) and for lithium (2).

The molecular weight of a dissolved substance is obtained from the equation $M = \frac{D \cdot m}{t - t_1}$. Assuming the molecular weight of gold to be identical with its atomic weight, we have, $197.2 = \frac{D \cdot 8.267}{4.38}$, whence $D =$ the molecular depression of the freezing point, in the case of sodium = 104.5.

Table V.

	Weight of metal per 100 grams Na.	Atoms of metal per 100 atoms Na.	$t - t_1$.	$\frac{104.5 \cdot m}{t - t_1}$.	Atomic weight.
	<i>m.</i>	<i>n.</i>			
Gold	8.267	0.965	4.38	197	197.2
Thallium	9.558	1.033	4.41	226	204.1
Mercury	7.368	0.847	3.83	201	200.0
Cadmium	2.649	0.544	1.95	142	112.4
Potassium	2.185	1.288	4.61	49.5	39.15
Lithium	0.3658	1.2	1.59	24	7.03
Li ₃	0.3658	0.4	1.59	24	21.09

From the preceding table, the following one has been calculated for the more or less well-known compounds of the dissolved metals with sodium. These compounds are described in the following papers: NaTl, Kurnakoff and Puschin;¹ NaHg and Na₃Hg, Kurnakoff² and Maey;³ the existence of

¹ Z. anorg. Chem., **30**, 86 (1902).

² *Ibid.*, **23**, 439 (1900).

³ *Loc. cit.*

NaK_2 is maintained by Joannis,¹ while Kurnakoff and Puschin² deny it and assert instead the existence of a compound of either the formula Na_2K or Na_3K_2 . The values found above do not agree for potassium itself, or for any of these compounds. The compound NaLi_3 is not mentioned in the literature. Its existence, however, would seem more probable than that of triatomic lithium molecules.

Table VI.

	<i>m.</i>	<i>n.</i>	$t-t_1$.	$\frac{104.5 \cdot m}{t-t_1}$.	Molecular weight.
NaTl	10.751	1.091	4.41	255	227.1
NaHg	8.285	0.856	3.83	226	223.0
Na_3Hg	10.173	0.871	3.83	277	269.1
NaK_2	2.847	0.647	4.61	64.5	101.3
Na_2K	4.883	1.324	4.61	110.7	85.2
Na_3K_2	4.196	0.656	4.61	95.1	147.4
NaLi_3	0.7686	0.401	1.59	50.5	44.1

Heycock and Neville's experiments were made as follows : Solid paraffin was first placed in the crucible and, as soon as it was melted, a weighed quantity of sodium (from 20 to 30 grams, in large sticks) was dropped in, the molten paraffin forming a layer above the sodium. The melting point of the sodium was then determined, after which small, weighed quantities of metal were added in succession. The melting point of the solution was determined after each addition.

From the last two tables it will be seen that their results do not indicate the non-existence of compounds of sodium with the dissolved metal. That Heycock and Neville did not realize this fact is shown by the following quotation :³

" When mercury was added to the molten sodium, a considerable evolution of heat and light took place. It is worthy of note that the atomic falls do not indicate in any way the formation of a chemical compound as might be anticipated. Had the mercury after addition appropriated a portion of the solvent, it should have made these atomic falls (?) increase as the number of atoms of solvent diminished. It seems not un-

¹ Ann. Chim. Phys., [6], 12, 358 (1887).

² Z. anorg. Chem., 30, 109 (1902).

³ Loc. cit., 55, 671.

reasonable to suppose that a compound may be formed at first and dissociated afterwards through the great dilution of the solution." Such a dissociation appears highly improbable.

That the metals dissolve in each other in the atomic condition was, apparently, further confirmed by the experiments of G. Meyer,¹ who measured the electromotive force of the combination :

Concentrated amalgam $\left| \begin{array}{l} \text{solution of a salt of} \\ \text{the dissolved metal} \end{array} \right|$ dilute amalgam.

From his results he calculated the molecular weight of the metal dissolved in mercury, by means of the equation

$$\pi = 0.002 \frac{T}{n} \log \frac{c_1}{c_2},$$

in which π = the electromotive force, T = the absolute temperature, n = the number of electrical units transported by one molecular weight of the metal in the form of ions, and c_1 and c_2 = the concentrations of the respective amalgams. By dividing n by the number of electrical units which go with one atom of the metal in question, Meyer calculated the number of atoms in the molecule and thence the molecular weight. For the metals investigated, *viz.* zinc, cadmium, lead, tin, copper and sodium, values were obtained which agree with their atomic weights. Barium was investigated by Schoeller² with the same result.

The formula of G. Meyer holds only when the dissolved metal, which must be more electropositive than mercury, exists as such in the latter. It does not apply to metals which form compounds with the mercury. In the case of sodium which, at ordinary temperatures, exists in solution as NaHg_8 , Haber³ has shown that the formula

$$\pi = 0.002T \left[\log \frac{c_1}{c_2} + 23.0 (c_1 - c_2) \right]$$

is applicable, and in his paper he demonstrates that the values experimentally obtained by Meyer in the case of sodium agree

¹ Z. physik. Chem., 7, 447 (1891).

² Z. elek. Chem., 5, 259 (1898).

³ Z. physik. Chem., 41, 399 (1902).

as well with the one formula as with the other. The results of Meyer's measurements for sodium amalgams are given here, together with the calculated values :

T.	c_1 .	c_2 .	Found.	Calculated.	
			Volt.	Meyer.	Haber.
293.2	0.0003325	0.0000953	0.0327	0.0315	0.0318
291.5	0.0002820	0.0000982	0.0248	0.0265	0.0267
285.0	0.0002282	0.0001006	0.0174	0.0196	0.0198

Almost simultaneously with Meyer's investigation, there appeared a theoretical paper by V. von Türlin,¹ in which was discussed the possibility of determining the molecular weights of metals dissolved in mercury, by measuring the electromotive force of the combination :

Mercury | solution of a mercurous salt | amalgam.

In this case the mercury is the transport metal, and equilibrium cannot be attained until all the mercury has dissolved and migrated to the amalgam. This, of course, presupposes that the salt of mercury shall not be acted upon by the amalgam ; *i. e.*, that the dissolved metal is more electronegative than mercury. This method, in connection with which, owing to the difficulty in procuring a suitable salt of mercury,² we have no experimental data, is fully analogous to the vapor-pressure method for determining molecular weights. In the latter case we have a depression of the vapor pressure, due to the dissolved metal, while in Türlin's combination we have a depression of the solution pressure, due to the same cause.³ The method of Türlin, like the vapor-pressure method, furnishes us with a possible means of determining, in the general formula M_nHg_m , the value of n . The value of m might, or might not be zero.

In this connection it may be mentioned that Coehn⁴ has recently prepared ammonium amalgam by the electrolysis of ammonium sulphate at 0°. The amalgam obtained at this temperature became only slightly inflated, and it retained its metallic appearance. Coehn showed that this amalgam is

¹ Z. physik. Chem., 5, 340 (1890).

² Cf. Meyer : *Loc. cit.*

³ Cf. Ostwald : "Lehrbuch," II., i, 863 (1903).

⁴ Z. anorg. Chem., 25, 430 (1900).

capable of precipitating copper, cadmium and zinc from well-cooled solutions of their sulphates, and thus established, beyond a doubt, that ammonium is capable of forming a true amalgam. The existence of free ammonium, or of di-ammonium, in this amalgam is, however, hardly to be assumed. We probably have to do here with a compound of mercury and ammonium, which, judging from the analogy that elsewhere exists between potassium and ammonium, probably has the formula $(\text{NH}_4)\text{Hg}_{12}$. At temperatures between 0° and 71° the compound KHg_{12} is stable.¹

Summary.

It has been shown, in the foregoing, that the methods for determining molecular weights which have been discussed do not furnish us with a means of deciding whether, in an amalgam or alloy, the dissolved metal is present as such, or in combination with the solvent. In the general formula M_nHg_m , these methods permit of the determination of n , but the degree of accuracy so far attained by these methods is not sufficient for determining the exact magnitude of m .

There is every evidence for the existence of many definite chemical compounds of mercury with the metals of the alkali and alkaline earth groups, and there is no reason to suppose that these compounds break up on being dissolved in mercury. The liquid amalgams of the metals of these two groups are solutions in mercury of compounds of the general formula MHg_m , containing only one atom of the amalgamated metal to the molecule.

In those cases in which we have good evidence for the non-existence of compounds of mercury with the dissolved metal, we are justified in concluding that the metal is dissolved, as such, in the mercury. This is the case with zinc, cadmium, bismuth, lead and tin and, according to the measurements of Ramsay, these metals exist, when dissolved in mercury, in the form of monatomic molecules.

UNIVERSITY OF ILLINOIS,
April 23, 1906.

¹ Kerp and Böttger : *Loc. cit.*

Contributions from the Sheffield Laboratory of Yale University.

CXXXI.—RESEARCHES ON PYRIMIDINES : THE ACTION OF POTASSIUM THIOCYANATE UPON IMIDE CHLORIDES.

[FIFTEENTH PAPER.]

BY TREAT B. JOHNSON AND ELMER V. MCCOLLUM.

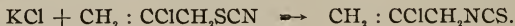
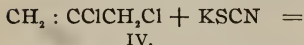
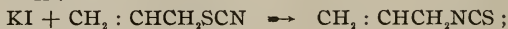
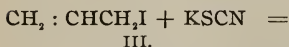
We shall describe in this paper a new case of the molecular rearrangement of a thiocyanate, I., to an isothiocyanate, II., which is unique for this type of metamerism.



In the acyclic series an unsaturated condition in the 2,3-position



is favorable for the formation of isothiocyanates. For example : Allyliodide, III., and 1,2-dichlorpropylene,¹ IV., when heated with potassium thiocyanate, react to form the corresponding isothiocyanates, according to the following equations :

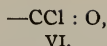
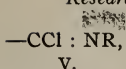


Such groupings, so far as examined, do not permit of the isolation of the primary products—thiocyanates—except when heat is avoided.

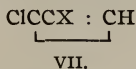
In a recent publication from this laboratory, Wheeler and Bristol² have described the behavior of some cyclic imide chlorides towards potassium thiocyanate. Since such chlorides, V., are closely related to acid chlorides, VI., and the cyclic

¹ Wheeler and Merriam : J. Am. Chem. Soc., 23, 287.

² THIS JOURNAL, 33, 448 (1905).

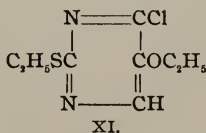
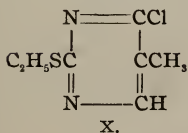
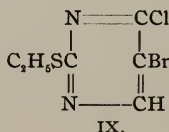
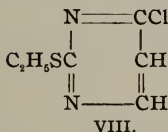
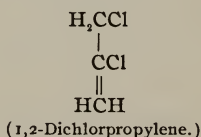
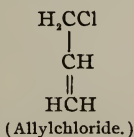


derivatives examined contain an unsaturated 2,3-position, VII.,



it seemed probable that isothiocyanates would result if such halides were treated with potassium thiocyanate.

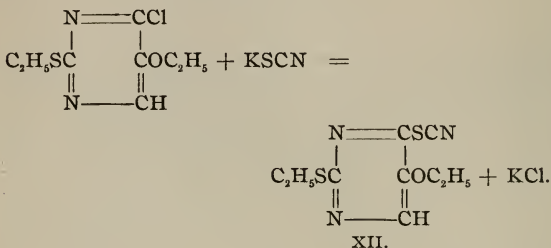
Their experimental data supported this assumption. They observed that 2-ethylmercapto-6-chlorpyrimidine, VIII., 2-ethylmercapto-5-brom-6-chlorpyrimidine, IX., and 2-ethylmercapto-5-methyl-6-chlorpyrimidine, X., reacted with potassium thiocyanate, under certain conditions, to give the corresponding isothiocyanates. They did not obtain any positive evidence of the intermediate formation of thiocyanates :



We had occasion to examine, in the course of our work, the behavior of 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine,¹ XI., towards potassium thiocyanate. On account of the close analogy of this imide chloride to those examined by Wheeler

¹ Johnson and McCollum : J. Biolog. Chem., 1, 437 (1906).

and Bristol,¹ we expected that it would react in a similar manner to form an isothiocyanate. We find that this chloride, XI., reacts smoothly with potassium thiocyanate, in an alcoholic solution, to give a normal rhodanide, XII., as represented in the following equation :



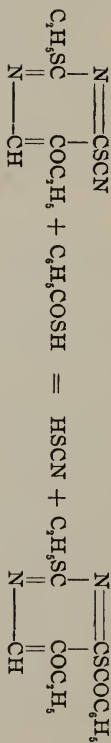
That a thiocyanate is the primary product of this reaction, we have established in the following manner: It did not give thiourea derivatives with ammonia or organic bases. It reacted quantitatively with thiobenzoic and thioacetic acids to give the same 2-ethylmercapto-5-ethoxy-6-thiopyrimidine, XIV. This reaction with thioacids involves the intermediate formation of 2-ethylmercapto-5-ethoxy-6-benzoylmercaptopyrimidine, XIII., and 2-ethylmercapto-5-ethoxy-6-acetylmercaptopyrimidine,² XV., which then undergo hydrolysis to the thiopyrimidine, XIV.

We find that 2-ethylmercapto-5-ethoxy-6-thiocyanpyrimidine, XII., shows no tendency to rearrange to the isothiocyanate,³ XVI., at the ordinary temperature. On the other hand, if heated above 100° it is transformed quantitatively into its isomer, XVI. The thiocyanate can be recrystallized from alcohol, but on prolonged boiling it partially rearranges to the isothiocyanate. This combines at once with the alcohol to form a urethane, XVII.

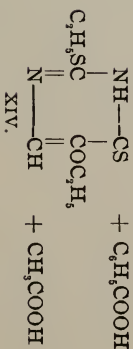
¹ *Loc. cit.*

² Wheeler and Merriam: *THIS JOURNAL*, 23, 283 (1901).

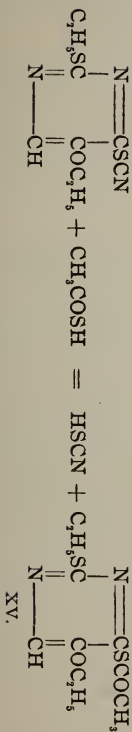
³ Samples of the thiocyanate that had been preserved for five months showed no change in melting point. We shall keep specimens for an indefinite period in order to see whether any rearrangement will take place at the ordinary temperature.



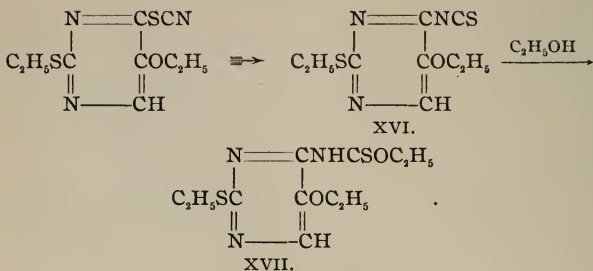
XIII.



XIV.

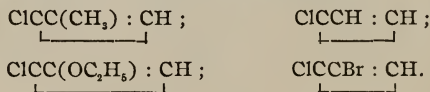


XV.



It seems very probable to the writers that the imide chlorides examined by Wheeler and Bristol¹ will give thiocyanates if treated with potassium thiocyanate under the proper conditions. Judging from the properties of 2-ethylmercapto-5-ethoxy-6-thiocyanpyrimidine, XII., their thiocyanates would be expected to undergo a rearrangement under the conditions employed in their experiments.

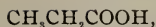
These four imide chlorides constitute an ideal series with which to test the rule as to whether the tendency for a thiocyanate to rearrange to an isothiocyanate is proportional to the negative character of the alkyl group. The only difference in structure is the character of the radicals occupying the 5-position. If the tendency to form isothiocyanates is directly proportional to the negative influence of these four radicals, evidently the negative character of the pyrimidines in question must be expressed by the following arrangement :



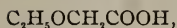
That the negative influence of the radicals occupying the 5-position is to be represented by the arrangement—CH₃, H, OC₂H₅, Br—is shown on substituting these groups in acetic acid and comparing the affinity constants² of the resulting acids.

¹ *Loc. cit.*

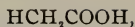
² Ostwald : *Phys. Chem.*, 3, 174-184.



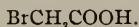
$$K = 0.00134$$



$$K = 0.0234$$



$$K = 0.0018$$

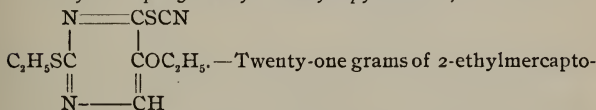


$$K = 0.138$$

The affinity constant in the case of acetic acid is decreased by the introduction of the methyl radical, while by the substitution of the more negative ethoxy group it is increased in the proportion 1 : 13. The investigation of these thiocyanate derivatives is now in progress in this laboratory.

EXPERIMENTAL PART.

2-Ethylmercapto-5-ethoxy-6-thiocyanpyrimidine,



5-ethoxy-6-chlorpyrimidine¹ and 11 grams of potassium thiocyanate were dissolved in 95 per cent alcohol and the solution boiled for 6 hours. Potassium chloride began to separate immediately on warming and by prolonged boiling the alcoholic solution assumed a red color. After the completion of the reaction the excess of alcohol was removed by evaporation and the residue treated with cold water, to extract the potassium chloride and the excess of potassium thiocyanate. We obtained a well crystallized product that was soluble in hot alcohol and benzene. It deposited from alcohol in lemon-yellow prisms, which melted, at 66°–67°, to a clear oil. When heated above its melting point it showed no signs of decomposition below 200°. It was insoluble in alkali and was not changed when warmed with aqueous ammonia. It possessed the properties of a weak base. It dissolved in strong hydrochloric acid and was reprecipitated unaltered by alkali or by dilution with water. Analysis (Kjeldahl) :

	Calculated for $\text{C}_9\text{H}_{11}\text{ON}_2\text{S}_2$.	Found.
N	17.42	17.12

¹ Johnson and McCollum : J. Biolog. Chem., 1, 443 (1906).

Action of Thiobenzoic Acid and Thioacetic Acid on 2-Ethylmercapto-5-ethoxy-6-thiocyanpyrimidine.

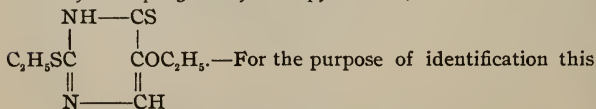
Two and five-tenths grams of the thiocyanate were dissolved in one molecular proportion of thiobenzoic acid. The substances reacted at once with the evolution of considerable heat. After warming for a few minutes in a boiling water-bath, to complete the reaction, the product was treated with a little alcohol, when it crystallized in the form of well developed, yellow prisms. It was purified for analysis by crystallization from alcohol. It melted, at 144° – 145° , to a clear oil. Nitrogen determinations agreed with the calculated value in *2-ethylmercapto-5-ethoxy-6-thiopyrimidine* (see below) :

	Calculated for $C_8H_{12}ON_2S_2$.	I.	Found. II.	III.
N	12.96	13.2	12.88	13.2

Two grams of the thiocyanate were dissolved, at the ordinary temperature, in 1 molecular proportion of thioacetic acid. After a few minutes heat began to be evolved and the mixture solidified. It was then warmed in a boiling water-bath for a few minutes. The product crystallized from 95 per cent alcohol in yellow prisms and melted, at 144° – 145° , to a clear oil. When this material was mixed with some of the compound obtained by the action of thiobenzoic acid on the thiocyanate, and heated in a capillary tube, the melting point was not lowered. The two substances were identical. We did not detect the formation of any carbon bisulphide in these reactions with thioacids.¹ When the mother liquors were treated with a solution of ferric chloride we obtained characteristic, red colored solutions, showing the presence of free thiocyanic acid. Analysis (Kjeldahl) :

	Calculated for $C_8H_{12}ON_2S_2$.	Found.
N	12.96	13.2

2-Ethylmercapto-5-ethoxy-6-thiopyrimidine,

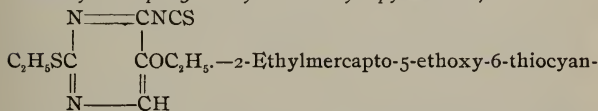


¹ Wheeler and Merriam : J. Am. Chem. Soc., 23, 284.

compound was prepared by boiling 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine with an alcoholic solution of potassium hydrosulphide. The reaction was smooth and potassium chloride precipitated at once from the alcohol. When the solution was acidified with acetic acid the pyrimidine separated as a yellow, crystalline substance. It deposited from alcohol in prisms and melted, at 144° – 145° , to a clear oil. When this material was mixed with the compounds obtained in the reactions with thioacids, described above, the melting point was not changed. Analysis:

	Calculated for $C_8H_{12}ON_2S_2$.	Found.
N	12.96	13.2

2-Ethylmercapto-5-ethoxy-6-isothiocyanypyrimidine,



pyrimidine shows no tendency to rearrange into the isothiocyanate at ordinary temperatures. In order to decide at what temperature this rearrangement would take place we performed the following experiments: One gram of the thiocyanate was heated in a sulphuric acid-bath, at 80° – 90° , for 1 hour. On cooling, the material crystallized immediately. It melted, at 66° – 67° , to a clear oil and was identified as the unaltered thiocyanate. It was then heated for another hour at 90° – 100° . The material solidified on cooling and melted sharply at 66° – 67° . It was then heated for 3 hours at 105° – 110° . On cooling the material refused to solidify and, after standing for several days, still retained the consistency of a syrup. That this product was an isothiocyanate was proved as follows: It reacted at once with ammonia to give practically a quantitative yield of 2-ethylmercapto-5-ethoxy-6-thioureapyrimidine (see below) which melted, at 171° – 172° , to a clear oil.

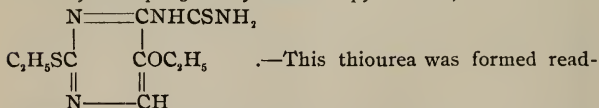
In order to obtain the isothiocyanate sufficiently pure for analysis, 10 grams of the thiocyanate were distilled under diminished pressure. Much decomposition took place, but we

obtained a fraction boiling at 228° – 235° (20–23 mm.). This oil was exceedingly hygroscopic and weighed 5 grams. When allowed to stand in a desiccator, over concentrated sulphuric acid, it finally solidified. It was exceedingly soluble in the common organic solvents and, when exposed to the air, began to assume an oily appearance. The crude material melted, at 45° – 50° , to a turbid oil. Analysis (Kjeldahl) :

	Calculated for $C_9H_{11}ON_3S_2$.	Found.
N	17.4	16.8

Two attempts were made to prepare this isothiocyanate by boiling a mixture of the chlorpyrimidine, toluene and potassium thiocyanate. In our first experiment 10 grams of the chlorpyrimidine and 5.5 grams of potassium thiocyanate were taken and the mixture boiled for 12 hours. Under these conditions we observed no evidence of any reaction. We then boiled a mixture of 5 grams of the chlorpyrimidine, 2.3 grams of potassium thiocyanate and toluene for 30 hours. On evaporating the excess of toluene and crystallizing the residue from petroleum ether, we recovered 4 grams of the unaltered chloride melting at 44° .

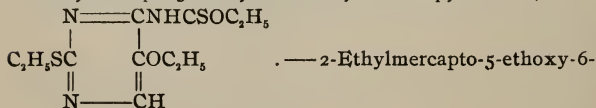
2-Ethylmercapto-5-ethoxy-6-thioureapyrimidine,



ily when the isothiocyanate above described was treated with aqueous ammonia. It deposited from hot alcohol in slender, yellow prisms, that melted at 172° , without effervescence, to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_9H_{14}ON_4S_2$.	Found.
N	21.70	21.47

2-Ethylmercapto-5-ethoxy-6-thionethylurethane pyrimidine,



thiocyanpyrimidine undergoes a rearrangement into the isomeric isothiocyanate derivative when boiled with alcohol. Thirty-five grams of 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine and 20 grams of potassium thiocyanate were dissolved in 95 per cent alcohol and the solution boiled for 11 hours. When we evaporated the alcohol and treated the residue with cold water, to remove potassium chloride and potassium thiocyanate, we obtained a semi-solid which showed no signs of crystallizing after standing for 3 hours. This material was then treated with a dilute solution of sodium hydroxide. We observed that part of the substance dissolved in the alkali and the insoluble portion assumed a crystalline form. This was filtered off and recrystallized from alcohol. It deposited in prisms that melted at 66° – 67° . It was identified as the thiocyanate. Analysis (Kjeldahl) :

	Calculated for $C_9H_{11}ON_3S_2$.	Found.
N	17.42	17.16

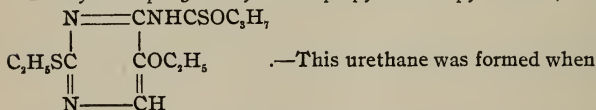
The urethane that was dissolved by the alkali was recovered when we acidified the solution with hydrochloric acid. It separated in light yellow prisms. It was insoluble in hot and cold water and very soluble in hot alcohol. It deposited from alcohol in long prisms, which showed signs of melting at 89° and then melted at 93° – 94° , to an oil. The yields of thiocyanate and urethane were about equal. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{17}O_2N_3S_2$.	Found.
N	14.63	14.85

In order to study the velocity of the rearrangement of the thiocyanate into its isomer in boiling ethyl alcohol, we performed the following experiments: Fifteen grams of 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine and 9 grams of potassium thiocyanate were boiled in alcohol for 24 hours. After separating the urethane from the thiocyanate in the usual way and then recrystallizing the compounds from alcohol, we obtained 1.2 grams of the thiocyanate and 10 grams of the urethane. In a second experiment we used 15 grams of the chlorpyrimidine, 9 grams of potassium thiocyanate and boiled the

alcoholic solution 4 hours. We obtained 10 grams of thiocyanate or 60.6 per cent of the theoretical, and 1.3 grams of urethane. In no case did our combined yields of thiocyanate and urethane correspond to more than 60-70 per cent of the theoretical. In order to demonstrate that this loss is due to the fact that the urethane slowly volatilizes when the alcoholic solutions are evaporated, we performed the following experiment: An alcoholic solution of 15 grams of the imide chloride and 6.6 grams of potassium thiocyanate was boiled for 30 hours. The alcoholic solution was then treated with a molecular proportion of sodium ethylate, to form a sodium salt of the urethane and evaporated to dryness. We obtained 4.9 grams of thiocyanate. The urethane was obtained by neutralizing its sodium salt with acetic acid and weighed 9.85 grams. These yields accounted for 95.26 per cent of the imide chloride used in the experiment.

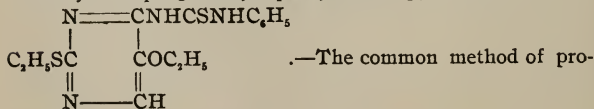
2-Ethylmercapto-5-ethoxy-6-thionpropylurethane-pyrimidine,



3 grams of 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine and 2 grams of potassium thiocyanate were dissolved in normal propyl alcohol and the solution boiled for 6 hours. Under these conditions we did not obtain any thiocyanate. The urethane was purified by recrystallizing from 95 per cent alcohol. It deposited in small prisms that melted, at 56°-57°, without effervescence, to a clear oil. Analysis (Kjeldahl):

N	Calculated for	Found.
	$\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}_3\text{S}_2$	
	13.95	13.76

2-Ethylmercapto-5-ethoxy-6-phenylthiourea-pyrimidine,



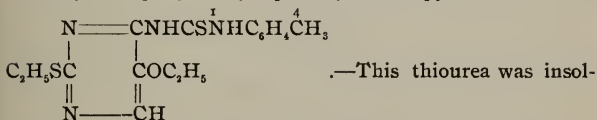
cedure in the preparation of the thioureas described in this

paper was to heat the 2-ethylmercapto-5-ethoxy-6-thiocyan-pyrimidine in an oil-bath at 150° – 160° , for about 30 minutes and thoroughly rearrange it to the isothiocyanate. This was then dissolved in a little benzene and combined with a molecular proportion of the organic base. The reactions were usually accompanied with evolution of heat and the yields of thioureas were practically quantitative.

The phenylthiourea derivative was soluble in hot alcohol and insoluble in water. It deposited from alcohol in distorted prisms and melted, at 82° – 83° , to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_{15}H_{18}ON_4S_2$.	Found.
N	16.76	16.75

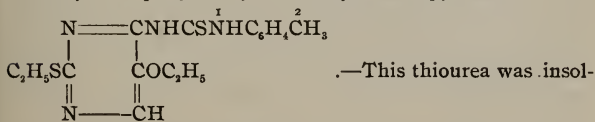
*2-Ethylmercapto-5-ethoxy-6-paratolylthiourea*pyrimidine,



uble in water. It was soluble in hot alcohol but insoluble in cold. It deposited from alcohol in clusters of needles radiating from a common center. They melted, at 115° , to a clear oil, without effervescence. Analysis (Kjeldahl) :

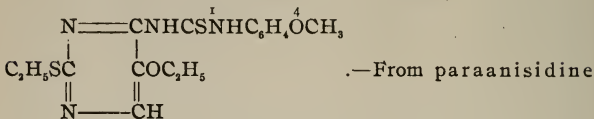
	Calculated for $C_{16}H_{20}ON_4S_2$.	Found.
N	16.09	16.20

*2-Ethylmercapto-5-ethoxy-6-orthotolylthiourea*pyrimidine,



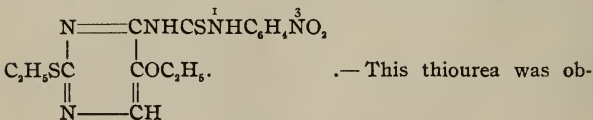
uble in water and soluble in warm alcohol. It deposited from alcohol in rhombic-shaped prisms and melted, at 129° – 130° , to a clear oil.

	Calculated for $C_{16}H_{20}ON_4S_2$.	Found.
N	16.09	15.86

2-Ethylmercapto-5-ethoxy-6-paraanisylthioureapyrimidine,

and 2-ethylmercapto-5-ethoxy-6-isothiocyanpyrimidine. This base showed little tendency to react with the isothiocyanate at ordinary temperatures. In order to complete the action the mixture was heated in a boiling water-bath, for 6 hours. The product was then washed with dilute hydrochloric acid to remove unaltered anisidine and afterwards purified by crystallizing from 95 per cent alcohol. It deposited from alcohol in rhombic prisms and melted at 122° – 123° . Analysis (Kjeldahl):

	Calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_4\text{S}_2$.	Found.
N	15.38	15.53

2-Ethylmercapto-5-ethoxy-6-metanitrophenylthioureapyrimidine,

tained when 1 gram of 2-ethylmercapto-5-ethoxy-6-isothiocyanate and a molecular proportion of metanitriline were dissolved in benzene and digested on the steam-bath, for 1 hour. When the benzene was evaporated the thiourea remained as an oil, which soon solidified. It was insoluble in hot water and slightly soluble in alcohol. It crystallized from benzene in the form of slender prisms which melted, at 161° , without effervescence, to a clear oil. Analysis (Kjeldahl):

	Calculated for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}_5\text{S}_2$.	I.	Found. II.	III.	IV.
N	18.47	18.23	18.23	18.09	18.10

NEW HAVEN, CONN.,
May 5, 1906.

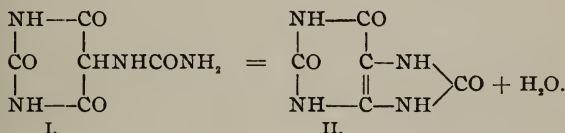
Contributions from the Sheffield Laboratory of Yale University.

CXXXII.—RESEARCHES ON PYRIMIDINES: ON THE
FORMATION OF PURINES FROM UREA-
PYRIMIDINES.

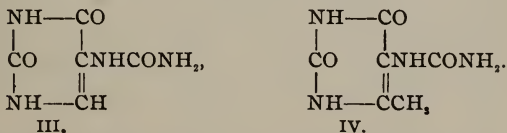
[SIXTEENTH PAPER.]

BY TREAT B. JOHNSON AND ELMER V. MCCOLLUM.

It has been shown by several investigators¹ that 5-urea-pyrimidines, in which the 4 and 6 positions are occupied by oxygen, I., condense to purines when heated with oxalic or hydrochloric acids. The condensation of 2,4,6-trioxy-5-urea-pyrimidine (pseudouric acid), I., to uric acid,² II., represents the simplest case of this method of purine formation.



On the other hand, 5-ureapyrimidines, III., IV., in which hydrogen or an alkyl radical occupies the 4-position, show no tendency to undergo a similar condensation when treated with dehydrating agents. Behrend³ obtained no evidence of the formation of purines when 2,6-dioxy-5-ureapyrimidine (hydroxyxanthine), III., and 2,6-dioxy-4-methyl-5-ureapyrimidine (methylhydroxyxanthine), IV., were treated, under various conditions, with phosphorus pentachloride, sulphuric acid, acetic anhydride and chlorsulphonic acid.

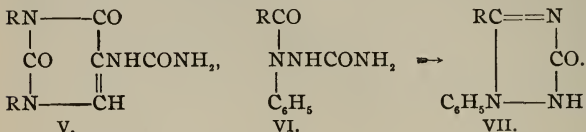


¹ Fischer and Ach: Ber. d. chem. Ges., 28, 2473. Fischer: *Ibid.*, 30, 559; 33, 1701. Sembritski: *Ibid.*, 30, 1814. Armstrong: *Ibid.*, 33, 2308.

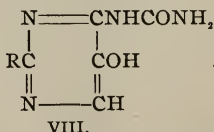
² Fischer and Ach: *Loc. cit.*

³ Ann. Chem. (Liebig), 229, 40; 231, 248, 251; 240, 1.

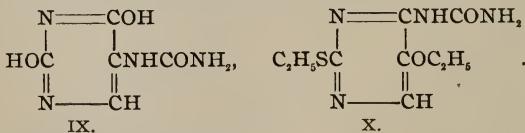
This observation of Behrend's was later confirmed by Widman.¹ He investigated the behavior of 2,6-dioxy-5-ureapyrimidines, V., towards potassium hydroxide. On account of the structural relationship between such ureapyrimidines and acylsemicarbazides, VI., it was important to compare their behavior towards this reagent. He found that the ureapyrimidines, V., could be recovered unaltered after warming with dilute solutions of potassium hydroxide, while the acylsemicarbazides, VI., condensed smoothly to triazoles,² VII.



On account of the pronounced difference in behavior of 4,6-dioxy-5-ureapyrimidines from 6-oxy-5-ureapyrimidines, III. and IV., it seemed desirable to prepare a 5-hydroxy-6-ureapyrimidine, VIII. It was of interest to decide whether such a ureapyrimidine derivative would undergo an inner condensation to form a purine.



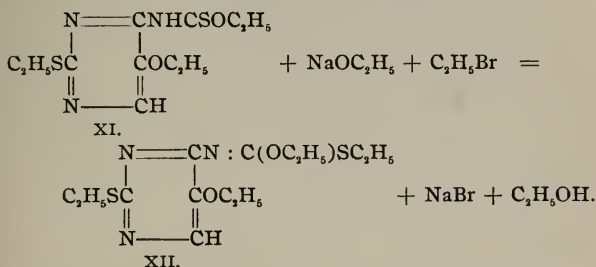
We have selected as a suitable representative of this new class of hydroxyureapyrimidines 2-ethylmercapto-5-ethoxy-6-ureapyrimidine, X. The structural relationship between this pyrimidine and Behrend's hydroxyxanthine, III., is illustrated by representing the oxygen derivative in its *enol* form, IX. :



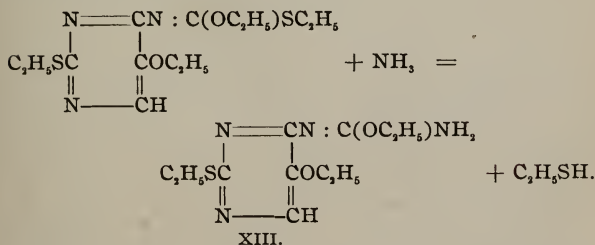
¹ Ber. d. chem. Ges., 29, 1954 (1896).

² Widman: Ber. d. chem. Ges., 29, 1946.

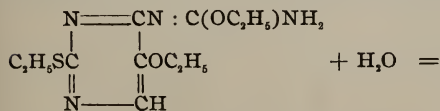
We have prepared this urea derivative, X., in the following manner: When 2-ethylmercapto-5-ethoxy-6-thionethylurethane-pyrimidine,¹ XI., was treated with molecular proportions of sodium ethylate and ethyl bromide, it gave 2-ethylmercapto-5-ethoxy-6-iminothioethylcarbonatepyrimidine, XII.:



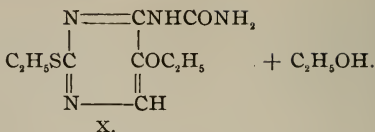
This iminothiocarbonate, XII., evolved ethylmercaptan when treated with alcoholic ammonia and was converted, practically quantitatively, into 2-ethylmercapto-5-ethoxy-6-pseudoethylureapyrimidine, XIII.:



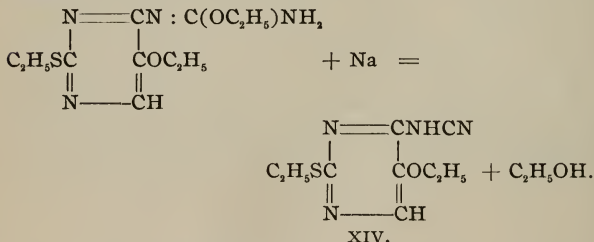
This pseudourea, XIII., then gave the normal urea, X., when treated with cold, concentrated hydrochloric acid:



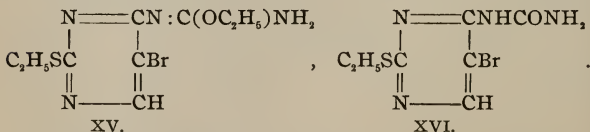
¹ Johnson and McCollum: THIS JOURNAL, 36, 136 (1906).



Attempts to condense the pseudourea, XIII., or the normal urea, X., to purine derivatives were without success. Sodium, in boiling benzene, attacked the pseudoureapyrimidine, XIII., to form a cyanaminopyrimidine, XIV. When the normal ureapyrimidine, X., was treated in the same manner it was recovered unaltered. It underwent decomposition when heated above its melting point :

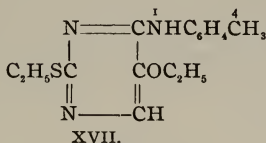


The 5-ethoxy radical in the above ureapyrimidines, XIII., and X., apparently is as firmly linked as the bromine atoms in the 5-brom-6-ureapyrimidines that were examined by Wheeler and Bristol.¹ They were unable to condense 2-ethylmercapto-5-brom-6-pseudoethylureapyrimidine, XV., or 2-ethylmercapto-5-brom-6-ureapyrimidine, XVI., to purine derivatives. The bromine atom in these compounds could not be removed by heating with pyridine, or by digesting in benzene with metallic sodium :



¹ THIS JOURNAL, 33, 448 (1905).

In this paper we also describe a series of substituted 6-aminopyrimidines that we have prepared by warming 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine¹ with organic bases. These derivatives are characterized by their stability towards boiling acids. 2-Ethylmercapto-5-ethoxy-6-paratoluidinopyrimidine, XVII., could be boiled with concentrated hydrochloric acid without removing the mercapto radical.



EXPERIMENTAL.

Diethylformylglycollate, $\text{C}_2\text{H}_5\text{OCH}(\text{CHO})\text{COOC}_2\text{H}_5$. — The sodium salt of this ester was described in a previous paper by Johnson and McCollum.² We now find that the free ester can easily be prepared from this sodium salt. It separated as a colorless oil when an aqueous solution of the sodium salt was acidified with hydrochloric acid. It was purified by fractional distillation, under diminished pressure. A fraction that distilled at $115^\circ\text{--}118^\circ$ (35 mm.) was used for the analytical determinations.

I. 0.4711 gram substance gave 0.8763 gram CO_2 and 0.3190 gram H_2O .

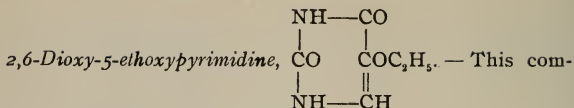
II. 0.4732 gram substance gave 0.8853 gram CO_2 and 0.3176 gram H_2O .

III. 0.4677 gram substance gave 0.8762 gram CO_2 and 0.3121 gram H_2O .

	Calculated for $\text{C}_7\text{H}_{12}\text{O}_4$.	I.	Found. II.	III.
C	52.5	50.72	51.02	51.09
H	7.5	7.33	7.45	7.41

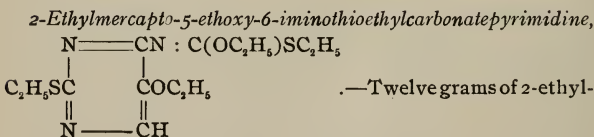
¹ Johnson and McCollum: *Loc. cit.*

² J. Biolog. Chem., 1, 437.



pound was described in a previous publication by Johnson and McCollum.¹ It was obtained, associated with isobarbituric acid, when 2-ethylmercapto-5-ethoxypyrimidine was heated in a sealed tube, with hydrochloric acid. We find that this pyrimidine can easily be prepared by boiling 2-methylmercapto-5-ethoxypyrimidine² with hydrochloric acid. It agreed in its properties with the compound described in our former paper. Analysis (Kjeldahl) :

	Calculated for $\text{C}_6\text{H}_8\text{O}_2\text{N}_2$.	Found.
N	17.95	18.00



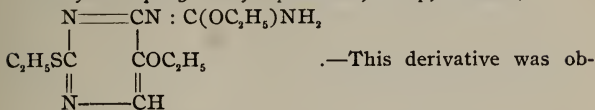
mercapto-5-ethoxy-6-thionethylurethanepyrimidine² were dissolved in alcohol containing one molecular proportion of metallic sodium. Four and five-tenths grams of ethyl bromide were then added and the solution allowed to stand at the ordinary temperature until neutral to litmus. After the reaction was complete the excess of alcohol was evaporated on the steam-bath, and the oily residue treated with cold water to remove sodium bromide. An oil was obtained which was extracted with ether and dried over calcium chloride. When the ether was evaporated, the diethylcarbonate remained as an oil which would not solidify. Analysis (Kjeldahl) :

	Calculated for $\text{C}_{13}\text{H}_{21}\text{O}_2\text{N}_3\text{S}_2$.	Found.
N	13.33	12.94

¹ *Loc. cit.*

² Johnson and McCollum : *Loc. cit.*

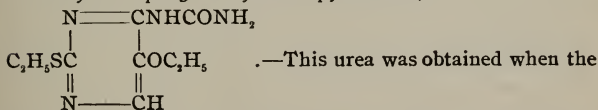
2-Ethylmercapto-5-ethoxy-6-pseudoethylureapyrimidine,



tained when dry ammonia gas was passed into an alcoholic solution of the above iminothioethylcarbonate. When the alcoholic solution was evaporated to dryness the pseudourea was obtained as a well crystallized compound. It was very soluble in alcohol and benzene and was purified for analysis by recrystallizing from ligroin. It melted, at 77° , to a clear oil. Analysis (Kjeldahl) :

	Calculated for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{N}_4\text{S}$.	Found.
N	20.74	20.40

2-Ethylmercapto-5-ethoxy-6-ureapyrimidine,



above pseudourea was allowed to stand dissolved in concentrated hydrochloric acid. After remaining a few days, the urea was precipitated by adding water. It was readily soluble in hot alcohol and deposited from cold alcohol in prismatic crystals, which melted at 166° – 167° , with slight effervescence, to a clear oil. It gave a strong test for sulphur, but did not contain chlorine. When mixed with 2-ethylmercapto-5-ethoxy-6-oxypyrimidine¹ (m. p. 166° – 167°) the melting point was lowered to 140° – 143° . Analysis (Kjeldahl) :

	Calculated for $\text{C}_9\text{H}_{14}\text{O}_2\text{N}_4\text{S}$.	Found.
N	23.14	23.17

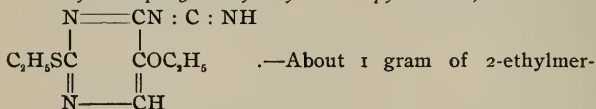
One gram of this urea and 1.5 grams of metallic sodium were suspended in benzene and the mixture boiled for 20 hours. There was no evidence of any reaction except that the sodium

¹ Johnson and McCollum : *Loc. cit.*

became coated with a thin deposit. When the benzene was evaporated and the sodium dissolved in alcohol, we obtained a crystalline deposit that melted at about 166°. It crystallized from hot, 95 per cent alcohol in prisms that melted at 166°–167°, with slight effervescence. It was identified as the unaltered urea. We did not observe the formation of the cyanaminopyrimidine (see below). Analysis (Kjeldahl) :

	Calculated for $C_9H_{14}O_2N_4S$.	Found.
N	23.14	23.07

2-Ethylmercapto-5-ethoxy-6-cyanaminopyrimidine,

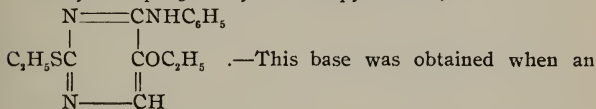


capto-5-ethoxy-6-pseudoethylureaprimidine was dissolved in dry benzene and treated with a slight excess over one molecular proportion of metallic sodium. The mixture was then boiled for 40 hours. The sodium underwent a complete change by this treatment and was transformed into a slimy precipitate. On filtering and evaporating the benzene there was no residue. The precipitate that remained on the filter was dissolved in alcohol and the solution evaporated to dryness. The residue was then dissolved in cold water. When this solution was acidified with acetic acid a white, crystalline product separated in the form of prisms. The substance melted sharply at 167°–168°, with only slight effervescence. It was soluble in alkali and was reprecipitated by acids. It was insoluble in cold, but readily soluble in hot water and alcohol. When dissolved in boiling water it slowly decomposed. On cooling it deposited in prismatic crystals that melted at about 165°–166°. When the cyanamide derivative (m. p. 167°–168°) was mixed with the above urea (m. p. 166°–167°) the melting point was lowered to 148°–155°. Analysis (Kjeldahl) :

	Calculated for $C_9H_{12}ON_4S$.	Found.
N	25.00	24.95

About 0.5 gram of the cyanamide derivative was allowed to stand dissolved in a few cc. of concentrated hydrochloric acid. A deposit of slender prisms was obtained which gave a strong test for chlorine. They melted at 175° – 180° , with violent effervescence, and had all the properties of a hydrochloric acid salt. On treating with dilute ammonia they completely dissolved, but on standing the solution deposited prismatic crystals that melted at 166° – 167° . This was identified as 2-ethylmercapto-5-ethoxy-6-ureaprimidine. When it was mixed with this urea the melting point was not lowered.

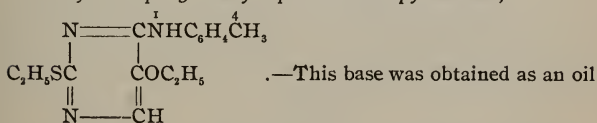
2-Ethylmercapto-5-ethoxy-6-anilino pyrimidine,



alcoholic solution of 3 grams of 2-ethylmercapto-5-ethoxy-6-chloropyrimidine and 2.8 grams of aniline were boiled for 24 hours. It was insoluble in water and very soluble in alcohol. It deposited from ligroin in large prisms, which melted at 60° . Analysis (Kjeldahl) :

	Calculated for $\text{C}_{14}\text{H}_{17}\text{ON}_3\text{S}$.	Found.
N	15.27	15.19

2-Ethylmercapto-5-ethoxy-6-paratoluidinopyrimidine,



when an alcoholic solution of 2-ethylmercapto-5-ethoxy-6-chloropyrimidine and the calculated quantity of paratoluidine was boiled for 10 hours. It formed a well crystallized hydrochloride, that deposited from water in hair-like crystals and melted at 105° – 106° , with effervescence. Analysis (Kjeldahl):

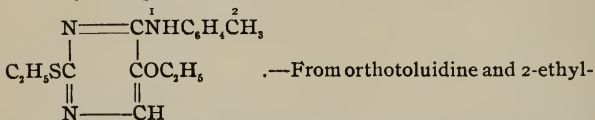
	Calculated for $\text{C}_{15}\text{H}_{19}\text{ON}_3\text{S} \cdot \text{HCl}$.	Found.
N	12.90	12.71

When the hydrochloride was treated with dilute ammonia the free base precipitated as an oil. It was soluble in ether and ligroin. It deposited from ligroin in long prisms, that melted at 72° . Analysis (Kjeldahl) :

	Calculated for $C_{15}H_{19}ON_3S$.	Found.
N	14.53	14.57

This mercaptopyrimidine can be boiled with concentrated hydrochloric acid without decomposition. After boiling 0.7 gram with an excess of hydrochloric acid, for 12 hours, it was recovered unaltered and melted sharply at 72° .

2-Ethylmercapto-5-ethoxy-6-orthotoluidinopyrimidine,



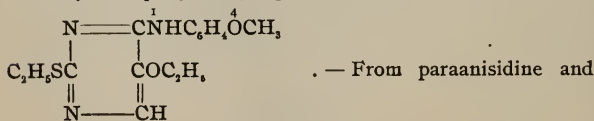
mercapto-5-ethoxy-6-chlorpyrimidine. Its hydrochloric acid salt crystallized from alcohol in prisms, that decomposed at 140° – 145° . The salt is not stable in aqueous solution and dissociates into the base and hydrochloric acid. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{19}ON_3S.HCl$.	Found.
N	12.90	12.30

The free base is insoluble in water, and very soluble in alcohol. It deposited from alcohol in flat prisms, that melted at 80° . It was insoluble in ligroin. Analysis (Kjeldahl) :

	Calculated for $C_{15}H_{19}ON_3S$.	Found.
N	14.53	14.49

2-Ethylmercapto-5-ethoxy-6-paraanisidinopyrimidine,



2-ethylmercapto-5-ethoxy-6-chlorpyrimidine. This reaction

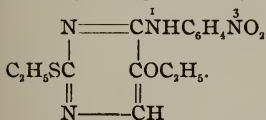
was not as smooth as those with the preceding amines. The base was first obtained as an oil which would not solidify. It was dissolved in dry benzene and the solution saturated with dry hydrochloric acid gas. The hydrochloride deposited in prismatic crystals. It was purified by recrystallization from acetone or ethyl acetate and was insoluble in benzene and ligroin. Analysis (Kjeldahl) :

	Calculated for $C_{15}H_{19}O_2N_3S.HCl.$	Found.
N	12.29	12.19

When the hydrochloride was treated with ammonia the base was obtained as an oil which finally solidified. It deposited from alcohol in stout prisms, that melted at 68° – 69° , without effervescence, to a clear oil. It was insoluble in water. Analysis (Kjeldahl) :

	Calculated for $C_{15}H_{19}O_2N_3S.$	I.	Found.	II.
N	13.77	13.77		13.81

2-Ethylmercapto-5-ethoxy-6-metanitroanilinopyrimidine,



.—The hydrochloride of this

pyrimidine base crystallized from alcohol and melted at 125° – 135° , with effervescence. The base was insoluble in water. It deposited from alcohol in long needles, which melted, at 125° , to a clear oil. Analysis (Kjeldahl) :

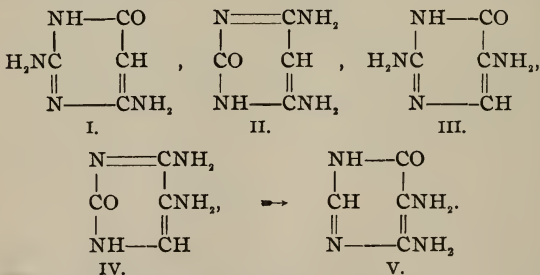
	Calculated for $C_{14}H_{16}O_2N_4S.$	Found.
N	17.50	17.13

CXXXIII. — RESEARCHES ON PYRIMIDINES: ON
5-NITROCYTOSINE AND ITS REDUCTION
TO 2-OXY-5,6-DIAMINOPYRIMIDINE.

[SEVENTEENTH PAPER.]

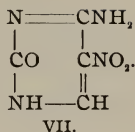
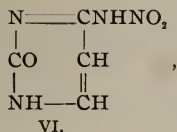
BY TREAT B. JOHNSON, CARL O. JOHNS AND FREDERICK W. HEYL.

There are five possible monooxydiaminopyrimidines in which the oxygen atom can occupy positions 2 and 6, assuming that the amino groups are attached to carbon. Their formulae are given below, I.-V. Three of these have been synthesized, *viz.* : 2,4-diamino-6-oxypyrimidine,¹ I., 2-oxy-4,6-diaminopyrimidine,² II., and 6-oxy-2,5-diaminopyrimidine,³ III. In this paper we shall describe the fourth member of this series — 2-oxy-5,6-diaminopyrimidine, IV. :



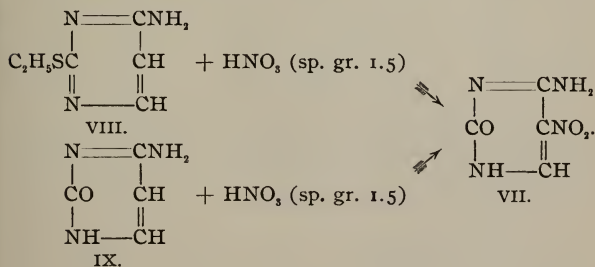
In a previous paper from this laboratory, Wheeler and Johnson⁴ have shown that cytosine is converted into nitrocytosine when treated with a mixture of nitric and sulphuric acids. No attempt was made to establish the structure of this nitro derivative. They assumed, nevertheless, on account of the unstable character of the products formed on reduction, that they were dealing with a nitramine, VI., instead of 5-nitrocytosine, VII. :

¹ Traube: Ber. d. chem. Ges., **33**, 1371.² Wheeler and Jamieson: THIS JOURNAL, **32**, 342 (1904).³ Johnson and Johns: *Ibid.*, **34**, 554 (1905).⁴ *Ibid.*, **31**, 591 (1904).



In the course of our work on oxydiaminopyrimidines it was necessary to decide whether the structure of nitrocytosine is to be represented by Formula, VI., or by Formula VII. If it is a 5-nitropyrimidine, VII., it seemed probable that it might give a diaminopyrimidine when reduced under the proper conditions.

The nitrocytosine that was used in this research was prepared by dissolving 2-ethylmercapto-6-aminopyrimidine,¹ VIII., in a mixture of concentrated nitric and sulphuric acids. It was converted, practically quantitatively, into the same nitropyrimidine, VII., as was obtained from cytosine,² IX.

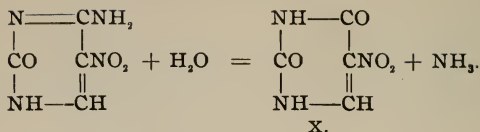


We now conclude that this nitro derivative is 2-oxy-5-nitro-6-aminopyrimidine, VII., and not a nitramine, VI., as represented in the previous paper.² That this conclusion is correct is established by the following data :

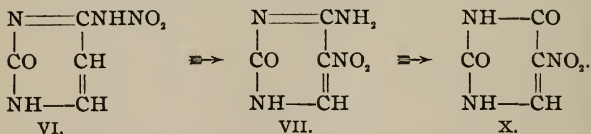
When nitrocytosine was heated under pressure, with 20 per cent sulphuric acid, it was converted into nitrouracil, X. :

¹ Wheeler and Johnson : *THIS JOURNAL*, 29, 497 (1903).

² Wheeler and Johnson : *Loc. cit.*



This result is analogous to those obtained when cytosine and 5-methylcytosine¹ were heated with sulphuric acid. They were converted into uracil and thymine, respectively. While this result supports the assumption that the nitro group in nitrocytosine occupies the 5-position, yet there was the possibility of the nitramine, VI., giving nitrouracil under the same conditions. This would involve a rearrangement of the nitro group from the amino radical to the 5-position in the pyrimidine ring, and then a hydrolysis to nitrouracil, as represented above :



Analogous rearrangements have been observed to take place in the benzene series. Bamberger² found, for example, that phenylnitramine, XI., was rearranged into orthonitroaniline, XII., when warmed with sulphuric or hydrochloric acids :



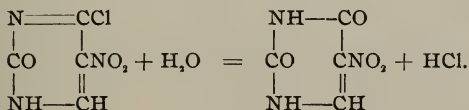
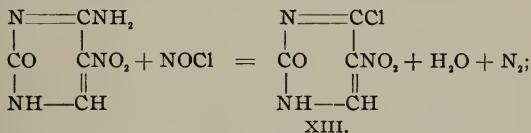
Although this rearrangement is theoretically possible, yet it did not seem probable to the writers because nitrocytosine is prepared under conditions that are not favorable for the forma-

¹ Wheeler and Johnson : *Loc. cit.*

² Ber. d. Chem. Ges. 26, 490.

tion of a nitramine. Furthermore, we have obtained experimental evidence which shows that this rearrangement does not take place.

It has been observed by several investigators¹ that the amino radical in amino acids is replaced by chlorine and bromine when these acids are treated with nitrosyl chloride and nitrosyl bromide. We have investigated the behavior of nitrosyl chloride towards nitrocytosine and find that this pyrimidine is converted smoothly into nitrouracil when warmed with an aqueous solution of the reagent.² This reaction involves the intermediate formation of 2-oxy-5-nitro-6-chlorpyrimidine, XIII. Under the conditions employed in our experiment this imide chloride, XIII., would be decomposed with the production of nitrouracil and hydrochloric acid, as follows :



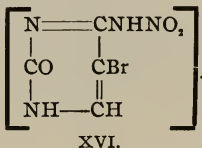
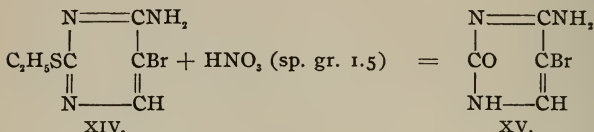
It appears to the writers that this method of formation of nitrouracil from nitrocytosine excludes the possibility of a rearrangement of the nitro group. The conditions of the reaction are far less favorable for a rearrangement than those employed in the preparation of nitrocytosine from 2-ethylmercapto-6-aminopyrimidine.

Furthermore, the following result would seem to indicate that there is no tendency for 2-mercapto-6-aminopyrimidines to form nitramines even when it is impossible for a nitro group to enter the 5-position in the pyrimidine ring. When 2-ethyl-

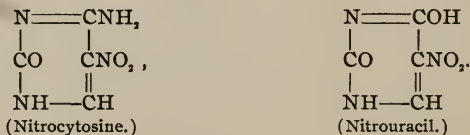
¹ Tilden and Forster : J. Chem. Soc., 67, 489. Tilden and Marshall : *Ibid.*, 67, 494. Walden : Ber. d. chem. Ges., 29, 134. Fischer : Ann. Chem. (Liebig), 340, 171. Stanek : Z. physiol. Chem., 46, 263 (1905).

² Stanek : *Loc. cit.*

mercapto-5-brom-6-aminopyrimidine,¹ XIV., was dissolved in a mixture of nitric and sulphuric acids it was converted, smoothly, into 5-bromcytosine,² XV. We obtained no evidence of the formation of a nitramine, XVI.



It has been the usual experience, when a pyrimidine having a hydrogen atom in the 5-position is attacked by bromine, that this hydrogen is easily replaced by the halogen.³ We now find that bromine has no action on nitrocytosine. This result is in accord with previous observations and again indicates that the nitro group occupies the 5-position in this pyrimidine. Behrend⁴ observed that nitrouracil was recovered unaltered after heating with liquid bromine, at 100°:



The above data and the facts that nitrocytosine does not

¹ Wheeler and Johnson: *THIS JOURNAL*, **31**, 604.

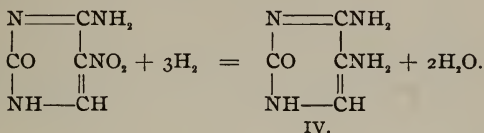
² Wheeler and Johnson: *Loc. cit.*

³ Wheeler and Johnson: *THIS JOURNAL*, **29**, 504. *Ibid.*, **31**, 603. Gabriel and Colman: *Ber. d. chem. Ges.*, **34**, 1238. Wheeler and Bristol: *THIS JOURNAL*, **33**, 437. Johnson and Johns: *Ibid.*, **34**, 175. *J. Biolog. Chem.*, **1**, 305.

⁴ *Ann. Chem. (Liebig)*, **240**, 11.

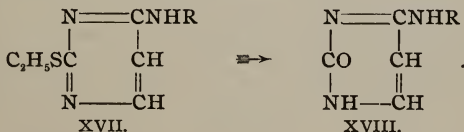
give "Liebermann's reaction,"¹ or 'Thiele and Lachman's'² "nitramine reaction," prove that nitrocytosine is a 2-oxy-5-nitro-6-aminopyrimidine, as represented by Formula VII.

We find that 5-nitrocytosine can be reduced with aluminium-amalgam to 2-oxy-5,6-diaminopyrimidine, IV. :



The reduction was very smooth, but we encountered several experimental difficulties before we succeeded in isolating the product. The base is especially characterized by the ease with which it undergoes decomposition in aqueous solution. It is the most unstable aminopyrimidine that we have prepared in this laboratory. It gave a very insoluble picrate and was precipitated from its aqueous solution by potassiobismuth iodide, mercuric chloride and phosphotungstic acid. Like 2,5-diamino-6-oxypyrimidine,³ it contained 1 molecule of water of crystallization.

In this paper we also describe a series of substituted 2-ethyl-mercapto-6-aminopyrimidines, XVII., that we have prepared by heating 2-ethylmercapto-6-chlorpyrimidine⁴ with aromatic bases. These mercaptopyrimidines were converted into cytosine derivatives, XVIII., when boiled with mineral acids :



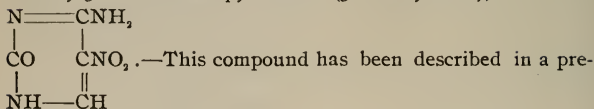
¹ Ber. d. chem. Ges., 7, 248. Baeyer: *Ibid.*, 7, 966. Mahla and Tiemann: *Ibid.*, 29, 2810. Frauesconi and Angelucci: Gazz. chim. ital., 31, II., 302 (1901). Scholl: Ann. Chem. (Liebig), 338, 3 (1904).

² Ann. Chem. (Liebig), 288, 269 (1895).

³ Johnson and Johns: *Loc. cit.*

⁴ Wheeler and Johnson: *Loc. cit.*

EXPERIMENTAL PART.

2-Oxy-5-nitro-6-aminopyrimidine (5-Nitrocytosine),

vious paper.¹ It was obtained by nitrating cytosine in the presence of sulphuric acid. We find that it can be obtained very easily by nitrating 2-ethylmercapto-6-aminopyrimidine.² The largest yield of nitrocytosine was obtained when we proceeded under the following conditions: Nineteen cc. of concentrated sulphuric acid were mixed with 37 cc. of nitric acid (sp. gr. 1.5). To this mixture were then slowly added 12.5 grams of the mercaptopyrimidine. The reaction was very violent and the pyrimidine dissolved immediately with evolution of much heat. After all the pyrimidine had been added the solution was allowed to stand at the ordinary temperature for about 15–16 hours. The mixture was then poured upon crushed ice and the acids neutralized with concentrated ammonia. The nitropyrimidine deposited from the neutral solution as a white, microscopic powder. It was purified by recrystallization from hot water. We obtained 10.5 grams of the nitropyrimidine, corresponding to 83.5 per cent of the theoretical yield. Analysis (Kjeldahl):

	Calculated for $\text{C}_4\text{H}_4\text{O}_3\text{N}_4$.	Found.
N	35.89	35.72

The Hydrochloride of 5-Nitrocytosine.—Nitrocytosine was dissolved in warm, dilute hydrochloric acid. Upon cooling, the hydrochloride deposited in clusters of needle-like prisms. They did not decompose below 300°. Analysis (Kjeldahl):

	Calculated for $\text{C}_4\text{H}_4\text{O}_3\text{N}_4 \cdot \text{HCl}$.	Found.
N	29.09	29.2

Behavior of 5-Nitrocytosine when Heated with Sulphuric Acid under Pressure.—Two grams of 5-nitrocytosine were heated in

¹ Wheeler and Johnson: *Loc. cit.*

² Wheeler and Merriam: *Loc. cit.*

a sealed tube, with 20 per cent sulphuric acid, for 3 hours, at 185° – 197° . When the tube was examined there was no pressure and slender prisms had deposited in the acid solution. They decomposed, with effervescence, at about 275° – 277° . The compound was insoluble in acids and soluble in ammonia and in sodium hydroxide. It gave no test for sulphuric acid when warmed with a solution of barium chloride, and agreed in its behavior with that of nitouracil. In order to demonstrate that it was nitouracil the material was reduced in an ammoniacal solution with aluminium amalgam. After filtering from aluminium hydroxide and concentrating the filtrate to a small volume, aminouracil deposited in needles. When a solution of the base was treated with picric acid we obtained the characteristic picrate of aminouracil. It sintered at 147° and then melted at 247° , with effervescence. Analysis of the free base:

	Calculated for $C_4H_5O_2N_3$.	Found.
N	33.06	32.9

Behavior of 5-Nitrocytosine when Heated with a Hydrochloric Acid Solution of Nitrosyl Chloride.—A solution of nitrosyl chloride was prepared according to the directions given by Stanek.¹ Three grams of nitrocytosine were heated in a sealed tube, with 40 cc. of the nitrosyl chloride solution, for 4 hours, at 85° – 95° . It was then allowed to stand at the ordinary temperature for 3 days. A clear solution resulted, which slowly evolved nitrogen. When the tube was opened there was considerable pressure and a crystalline precipitate was suspended in the solution. This was difficultly soluble in hot water. It deposited, on cooling, in clusters of radiating prisms. They had no definite melting point but decomposed, without melting, when heated above 250° . It was insoluble in acids, soluble in alkalis and did not respond to a test for chlorine. A nitrogen determination agreed with the calculated value in nitouracil (Kjeldahl):

	Calculated for $C_4H_5O_4N_3$.	Found.
N	26.75	27.00

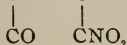
¹ Z. physiol. Chem., 46, 265.

Action of Nitric Acid on 2-Ethylmercapto-5-brom-6-aminopyrimidine.—This mercaptobrompyrimidine¹ was nitrated under practically the same conditions as were employed in the preparation of 5-nitrocytosine from 2-ethylmercapto-6-aminopyrimidine. Eight cc. of nitric acid (sp. gr. 1.5) were mixed with 4 cc. of concentrated sulphuric acid. Two and five-tenths grams of the mercaptopyrimidine were then slowly added to this acid mixture. Much heat was evolved and the mercaptopyrimidine dissolved at once, but the reaction was not as violent as in the nitration of 2-ethylmercapto-6-aminopyrimidine. After standing for 12 hours the solution was poured upon crushed ice and the acids neutralized with ammonia. When the liquid was concentrated to a volume of 25 cc. and cooled, a microscopic powder deposited. The material was purified by crystallization from hot water. It decomposed, without melting, when heated above 230°. It contained bromine but did not respond to a test for sulphur. A nitrogen determination agreed with the calculated value in 5-bromcytosine (Kjeldahl) :

	Calculated for $C_4H_4ON_3Br$.	Found.
N	22.10	22.17

Action of Bromine on 5-Nitrocytosine.—This pyrimidine was not attacked by bromine. It was suspended in glacial acetic acid and treated with a large excess of bromine. There was no apparent change after standing for 2 days. More bromine was then added to the acetic acid and the solution warmed in a water-bath. Under these conditions no hydrobromic acid was evolved and the nitrocytosine was recovered unaltered.

2-Oxy-5-nitro-6-phenylureaprimidine,



.—Molecular proportions of finely

pulverized 5-nitrocytosine and phenylisocyanate were heated together, at 100°, for several hours. The reaction was, apparently, perfectly smooth. When it was complete the urea

¹ Wheeler and Johnson : *Loc. cit.*

was washed with alcohol, to remove any unaltered phenylisocyanate and then with cold, 20 per cent hydrochloric acid, to remove unaltered nitrocytosine. It was then thoroughly washed with water and dried at 100°. It was practically insoluble in all solvents and slowly decomposed, without melting, when heated above 215°. Analysis (Kjeldahl) :

	Calculated for $C_{11}H_9O_4N_5$.	Found.
N	25.45	25.9

Action of Acetic Anhydride on Nitrocytosine.—5-Nitrocytosine does not react in a smooth manner with acetic anhydride. When boiled with the anhydride it slowly dissolves to a yellow solution that assumes a red color on prolonged boiling. Different products are formed by this treatment and in varying proportions, depending upon the quantity of anhydride used and on the length of time of boiling. In every experiment that we performed we invariably obtained mixtures of a monoacetyl and a diacetyl derivative, with unaltered material. It was extremely difficult to obtain conditions favorable for the formation of a single acetyl compound.

In one experiment 0.5 gram of nitrocytosine was dissolved in 8 cc. of boiling acetic anhydride. The solution was then immediately cooled, when we obtained a deposit of lenticular shaped crystals. They were soluble in hot water and deposited, on cooling, in prisms. When crystallized a second time the material deposited in fern-like forms that began to darken at 205° and decomposed at about 260°, without effervescence. Analysis (Kjeldahl) :

	Calculated for $C_8H_6O_4N_4$.	Found.
N	28.28	28.35

In two other experiments we duplicated the above conditions, except that we boiled the anhydride solution for a longer time. We obtained material that deposited from water in prismatic crystals. While the crystalline form suggested purity, the melting points were unsatisfactory and the nitrogen determinations indicated that we were dealing with a mixture of about equal proportions of a monoacetyl and a diacetyl

derivative. The material that was analyzed decomposed at 206°–208°, with effervescence.

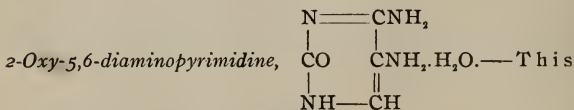
	Calculated for $C_6H_6O_4N_4$.	Calculated for $C_8H_8O_6N_4$.	Average.	I. Found.	II.
N	28.28	23.33	25.8	26.0	25.81

In another experiment we used freshly distilled acetic anhydride. One and seven-tenths grams of the nitropyrimidine were suspended in 10 cc. of the anhydride and the mixture boiled until the pyrimidine completely dissolved. Upon cooling, 1.3 grams of material deposited. It was difficultly soluble in hot water and deposited, on cooling, in needle-like prisms that decomposed at 273°–275°, with violent effervescence. A nitrogen determination agreed with the calculated value for a diacetyl derivative :

	Calculated for $C_8H_8O_6N_4$.	Found.
N	23.33	23.23

The original anhydride filtrate was allowed to evaporate to dryness. We obtained a crystalline residue that proved to be a mixture. After several recrystallizations from water we finally isolated a product that possessed all the properties of the original 5-nitrocytosine. Analysis (Kjeldahl) :

	Calculated for $C_4H_4O_3N_4$.	Found.
N	35.89	35.3



pyrimidine was formed by reducing 5-nitrocytosine with aluminium amalgam. We had great difficulty in preparing this base and it was only after obtaining negative results from several experiments that we eventually found conditions under which it was possible to isolate it. We finally succeeded in making the compound in the following manner: Three grams of finely pulverized 5-nitrocytosine were suspended in cold water, in contact with aluminium amalgam. The temperature of the solution was not allowed to rise above 35° during the reduction, and the

mixture was thoroughly agitated in order to disintegrate the coarser particles of the nitropyrimidine. In about 30 minutes the nitropyrimidine had completely dissolved and the reduction was complete. During the reduction we did not detect the presence of ammonia, but after the reduction was finished it was noticeable, indicating a partial decomposition of the diamino derivative. In order to avoid decomposition we quickly filtered from aluminium hydroxide, when we obtained a clear, straw-colored solution. This gradually assumed a dark color when exposed to the air. In order to isolate the pyrimidine base, the solution was concentrated to a small volume by slow evaporation, under diminished pressure. The temperature was kept below 50° and a slow stream of dry hydrogen was passed continually through the capillary tube to avoid oxidation. Considerable amorphous material deposited. After concentrating to about 10 cc., the dark colored solution was filtered and allowed to stand in an ice chest, for 2 days. We obtained a deposit of amorphous substance associated with clusters of radiating prisms. The prisms were carefully removed and washed with cold water. They decomposed when heated above 230° and contained water of crystallization. For analysis they were dried in the atmosphere.

The water of crystallization was determined by heating at 120° – 130° , for 1 hour.

0.1124 gram substance lost 0.0163 gram H_2O .

	Calculated for $C_4H_6ON_4 \cdot H_2O$.	Found.
N	12.50	14.50

A determination of nitrogen in the anhydrous material gave the following result (Kjeldahl).

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	44.00

This base was, apparently, quite stable after drying in the air, but when dissolved in water it slowly decomposed with separation of amorphous material. It behaved in every respect like an orthodiamine. An aqueous solution of the base gave the following characteristic reactions: Potassiobismuth iodide

gave an insoluble, red precipitate; platinum and gold chlorides were reduced to metallic platinum and gold; Fehling's solution was reduced at once, and a silver mirror was formed when a solution of the base was added to an ammoniacal solution of silver nitrate.

An aqueous solution of the base gave an alkaline reaction when tested with turmeric and litmus. The base gave no difficultly soluble salts with nitric, hydrochloric and sulphuric acids. It was precipitated by phosphotungstic acid.

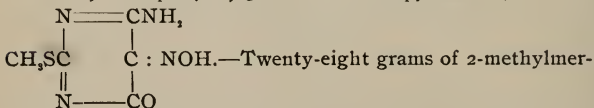
The Picrate of 2-Oxy-5,6-diaminopyrimidine.—This salt deposited from hot water in balls of microscopic prisms. The crystalline form resembled very much that of uracil. It had no definite melting point, but began to turn brown at about 170° , slowly decomposed on further heating, and did not effervesce at 300° . Analysis (Kjeldahl) :

	Calculated for $C_4H_6ON_4 \cdot C_6H_3O_7N_3$.	I.	Found. II.
N	27.60	27.67	27.50

The Mercuric Chloride Salt.—This was obtained when mercuric chloride was added to a solution of the base. Analysis (Kjeldahl) :

	Calculated for $C_4H_6ON_4 \cdot HgCl_2$.	Found.
N	14.1	13.89

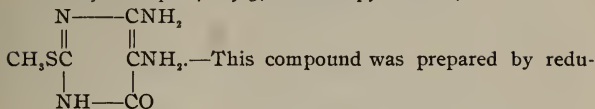
2-Methylmercapto-4-oxy-5-nitroso-6-aminopyrimidine,



capto-4-oxy-6-aminopyrimidine¹ and 7.2 grams of sodium hydroxide were dissolved in 450 cc. of water. To this solution was added a concentrated solution of 14 grams of sodium nitrite and then, slowly, 24 grams of glacial acetic acid. The mixture was allowed to stand for 2 hours, when the nitroso derivative deposited as a yellow, crystalline precipitate. After thoroughly washing with cold water, alcohol and ether the crude material was used for the following preparation :

¹ Johnson and Johns: *Loc. cit.*

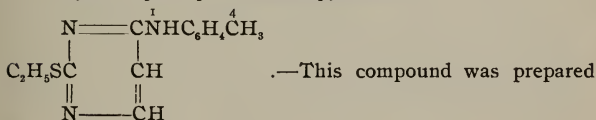
2-Methylmercapto-4-oxy-5,6-diaminopyrimidine,



cing the above nitroso derivative with ammonium sulphide. The base deposited from water in needle-like prisms that melted at 215° – 216° , with effervescence. It was very soluble in alcohol. It was unstable and gradually assumed a red color when exposed to the air. Analysis (Kjeldahl) :

	Calculated for $\text{C}_5\text{H}_8\text{ON}_4\text{S}$.	Found.
N	32.55	32.15

2-Ethylmercapto-6-paratoluidinopyrimidine,

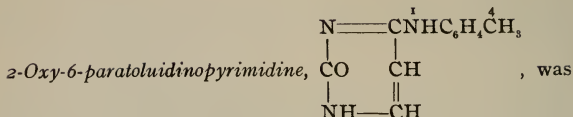


by dissolving 2-ethylmercapto-6-chlorpyrimidine and paratoluidine in dry benzene, in the proper proportions, and warming the solution for several hours on the steam-bath. The excess of benzene was then evaporated on the steam-bath and the pyrimidine purified in the form of its hydrochloride. This deposited from dilute hydrochloric acid in needles that decomposed at 198° – 207° , with effervescence. The salt was soluble in hot alcohol and deposited, on cooling, in needles. Analysis (Kjeldahl) :

	Calculated for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S} \cdot \text{HCl}$.	Found.
N	14.92	14.87

The free base was obtained when the hydrochloride was treated with aqueous ammonia. It separated as a pasty mass, which finally solidified. It deposited from petroleum ether in prismatic crystals that melted, at 104° , to a clear oil. They were extremely soluble in alcohol and benzene. Analysis (Kjeldahl) :

	Calculated for $C_{18}H_{15}N_3S$.	Found.
N	17.14	16.93



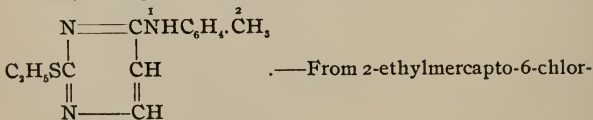
obtained in the form of its hydrochloride by boiling 2-ethylmercapto-6-paratoluidinopyrimidine with concentrated hydrochloric acid until ethylmercaptan ceased to be evolved. It deposited from alcohol in microscopic prisms that decomposed between 180° – 190° , with effervescence. It was soluble in hot water. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3.HCl$.	Found.
N	17.68	17.81

When an aqueous solution of this hydrochloric acid salt was treated with ammonia the free base separated as a crystalline precipitate. It was insoluble in hot water and the ordinary organic solvents, but was purified for analysis by prolonged extraction with hot water. It decomposed slowly when heated above 280° and then melted, to a dark colored oil, at 288° – 289° , with violent effervescence. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	20.71

2-Ethylmercapto-6-orthotoluidinopyrimidine,

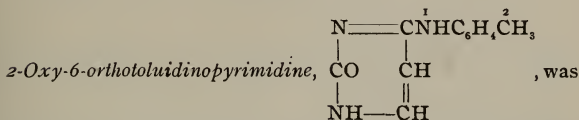


pyrimidine and orthotoluidine. Its hydrochloride deposited from dilute hydrochloric acid in granular crystals that melted at 230° – 232° , with effervescence. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{15}N_3S.HCl$.	Found.
N	14.92	14.63

When an aqueous solution of the hydrochloride was treated with ammonia the base separated as an oil which solidified on standing. It deposited from alcohol in prisms that melted, at 87° , to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_{13}H_{15}N_3S$.	Found.
N	17.14	17.04



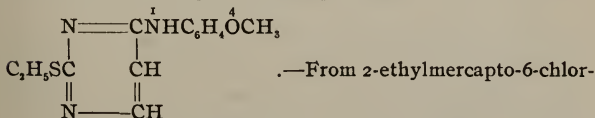
prepared by boiling 2-ethylmercapto-6-orthotoluidinopyrimidine with hydrochloric acid. The hydrochloride was very soluble in water but insoluble in benzene and acetone. It was purified for analysis by crystallizing from 95 per cent alcohol. It deposited in lenticular shaped crystals that decomposed at 227° - 231° , with effervescence. Analysis (Kjeldahl) :

	Calculated for $C_{11}H_{11}ON_3.HCl$.	Found.
N	17.68	17.35

The pyrimidine base was insoluble in cold water. It deposited from hot water in radiating prisms that decomposed at 262° . Analysis (Kjeldahl) :

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	21.05

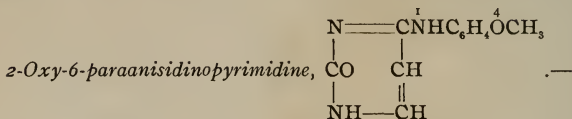
2-Ethylmercapto-6-paraanisidinopyrimidine,



pyrimidine and paraanisidine. The hydrochloride of this base deposited from hot water in needles that melted at 200° - 201° , with effervescence, to an oil. Analysis (Kjeldahl) :

	Calculated for $C_{13}H_{15}ON_3S.HCl$.	Found.
N	14.11	14.11

When the salt was treated with ammonia the base was obtained as an oil, that did not solidify after standing for several weeks.



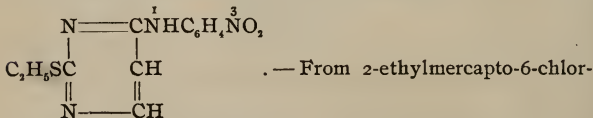
The hydrochloride deposited from water in small, radiating needles. It was purified for analysis by recrystallizing from alcohol that was acidified with hydrochloric acid. It decomposed between 145° and 165° , with effervescence. Analysis (Kjeldahl):

	Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3\cdot\text{HCl}$.	I.	Found.	II.
N	16.56	16.72		16.65

The free base was difficultly soluble in all ordinary media and showed no crystalline form. It was purified for analysis by drying at 110° , for 2 hours. It melted at 262° . Analysis (Kjeldahl):

	Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$.	I.	Found.	II.
N	19.35	19.68		19.53

2-Ethylmercapto-6-metanitroanilinopyrimidine,



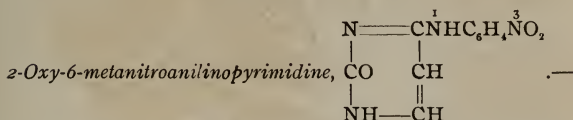
pyrimidine and metanitroaniline. In this experiment we observed that the free base could be more easily purified than its hydrochloric acid salt. It was insoluble in water and soluble in alcohol. It melted at 175° . Analysis (Kjeldahl):

	Calculated for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_4\text{S}$.	I.	Found.	II.
N	20.29	20.6		20.13

The hydrochloride was prepared by dissolving the base in dilute hydrochloric acid. It deposited in needles that decom-

posed at 140°–155°, with effervescence. Analysis (Kjeldahl):

N	Calculated for $C_{12}H_{12}O_2N_4S \cdot HCl$.	Found.	
	I.	II.	
	17.92	17.5	17.67



This compound could not be obtained in the usual manner by boiling the above 2-ethylmercapto-6-metanitroanilinopyrimidine with hydrochloric acid. The mercaptopyrimidine was recovered unaltered after boiling with concentrated hydrochloric acid for 15 hours. In order to remove the mercapto radical it was necessary to boil with hydrobromic acid. The hydrobromide was purified by crystallization from 95 per cent alcohol. It decomposed between 160° and 180°, with effervescence. When the salt was treated with alcoholic ammonia the pyrimidine base separated in needle-like prisms. They decomposed when heated above 275°. Analysis (Kjeldahl):

N	Calculated for $C_{10}H_8O_2N_4$.	Found.
	I.	II.
	24.14	24.35

NEW HAVEN, CONN.,
June 1, 1906.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

IX. REACTIONS WITH STEREOISOMERS.

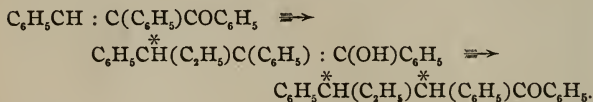
BY E. P. KOHLER.

In the last paper¹ it was shown that two racemic products are obtained whenever the addition of an organic magnesium compound to an unsaturated nitrile results in substances containing two unequal, asymmetric carbon atoms. Most of the substances of this type have heretofore been made by one of two methods; by addition to ethylene derivatives, or by the inter-

¹ THIS JOURNAL, 35, 386.

action of two substances of which each contained one asymmetric carbon atom. By the first of these methods the two asymmetric carbon atoms are generated simultaneously ; two racemic modifications are formed, but generally in very unequal quantities. It is known¹ that the second method also gives two racemic modifications, but there are no results that show the relative amounts.

When substances containing two asymmetric carbon atoms are obtained by the addition of Grignard's reagent to unsaturated compounds, the asymmetry is established in steps :



For the purpose of explaining the mechanism of 1,4-addition it is important to determine, as far as possible, the manner in which the asymmetry is produced. The possibilities are as follows :

1. The addition of the reagent results in the formation of two ethylene isomers which, on rearrangement, pass into the corresponding optical antipodes. The direct product of addition would, in this case, contain four substances, because each ethylene isomer would be a racemic modification containing one asymmetric carbon atom.

2. The addition product contains but one racemic ethylene derivative, the two components forming two pairs of antipodes during rearrangement.

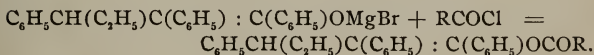
3. The entire reaction results in but one racemic modification, the second being due to autoracemization, which takes place very readily when an asymmetric carbon atom holds mobile hydrogen.

These possibilities could not be examined with the nitriles discussed in the previous paper, because the results are complicated by the presence of the triple linkage in cyanogen. It was necessary, therefore, to repeat the experiments, using ketones in place of nitriles, and in order to make the results as

¹ Kipping and Salway : J. Chem. Soc., 85, 438.

general as possible it was desirable to use ethylene isomers. Benzal- and *iso*-benzaldehyoxybenzoin, the best known pair of stereoisomeric ketones, were found to serve admirably for this purpose. Nearly all the reactions are perfectly clean and the products solids, hence it was possible to account for all of the materials used.

To test the first assumption, equal quantities of the two ketones were added to ethylmagnesium bromide, in carefully cooled and in boiling ethereal solution. As the resulting magnesium derivatives could not be examined directly, it was necessary to transform them into more stable substances with the same structure. For this purpose the ethereal solutions were cooled in freezing mixtures and treated with acid chlorides:



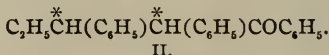
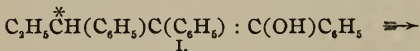
The same acyl derivative was obtained, in calculated quantity, from both ketones. This result indicates that but one magnesium derivative is formed, because it is improbable that, under the conditions of the experiment, the reaction with acid chlorides is accompanied by rearrangement. Other results described below lead to the same conclusion.

To test the second assumption, both the magnesium and the acyl derivatives were hydrolyzed. All of these substances should give the diphenylbutyrophenone, of which two racemic modifications were described in an earlier paper. It was found that when the magnesium derivative is decomposed with ice water, in the usual way, 80 per cent of the product consists of the low-melting and the remainder of the high-melting modification of this ketone, while the acetyl and benzoyl derivatives, on hydrolysis with acids or bases, give only the high-melting modification. The apparent contradiction between these results was removed by the discovery that the low-melting ketone passes into its isomer so readily, that only the latter could be expected when the acyl derivatives are hydrolyzed by boiling with acids or bases.

The unusual ease with which one of these ketones is trans-

formed into the other suggests the possibility that the low-melting ketone is the sole product formed by decomposing the magnesium derivative, and that the relatively small quantity of the high-melting isomer is due to subsequent racemization, I believe that such is the case, for although it was not possible to direct the reaction in such a way as to get only one product, it was found that the relative amounts of the two ketones obtained depend entirely upon the mode of hydrolysis, and that when the conditions are least favorable to racemization the yield of high-melting ketone is less than 0.5 per cent.

It is probable, therefore, that but one substance is formed in the process :



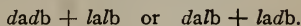
It is not difficult to explain such a result. The ethylene derivative (I.) is composed of two optical isomers containing one asymmetric carbon atom. In the sugars, as Fischer discovered,¹ additions to optically active substances may take place asymmetrically, the active group exercising a directing influence upon the addend. Later observations,² and particularly the recent success³ in achieving "asymmetric synthesis," indicate that this mode of addition is not exceptional. It is probable, therefore, that in a rearrangement like that under consideration, the active group containing the asymmetric carbon would exercise a similar influence upon the shifting hydrogen. This would necessarily give the result obtained. If we represent the two asymmetric carbon atoms in the product by a and b, and the ethylene derivative by *da* + *la*, then the ketone obtained from *da* may be either *dadb* or *dalb*. If the former represents the product from *da*, then the product from *la* must be *lalb*, because the directive influence is opposite in character. Similarly, if the product in the first case is *dalb*,

¹ Ber. d. chem. Ges., 22, 370. Ann. Chem. (Liebig), 270, 68.

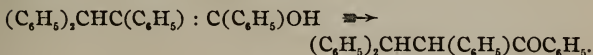
² Ber. d. chem. Ges., 37, 2486.

³ J. Chem. Soc., 85, 1249; 87, 1373; 89, 365.

then the product from *la* must be *ladb*. In either case only one inactive substance should be obtained :



A study of oxymethylene compounds, led Claisen¹ to the conclusion that the presence of phenyl groups in certain positions favors enolic modifications. To account for the anomalous behavior of diphenylacetaldehyde, for example, he suggested the formula $(C_6H_5)_2C:CHOH$ instead of $(C_6H_5)_2CHCHO$. Similarly Biltz,² after a careful investigation of triphenylethane derivatives, suggested that the substance previously regarded as diphenylacetophenone was, in reality, an enolic compound, $(C_6H_5)_2C:C(C_6H_5)OH$, instead of $(C_6H_5)_2CHCOC_6H_5$. In view of these conclusions it seemed worth while to try to isolate some of the enols which, as I have assumed, are formed when the magnesium derivatives, obtained from unsaturated compounds, are decomposed with water. Only one of the many experiments made in this direction was completely successful. In the case of tetraphenylpropenol it was possible to isolate the pure substance in crystalline form, to prove its structure, and to observe the transition into the isomeric triphenylpropionophenone :

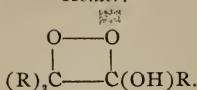


In other cases, where the enols could not be obtained in a solid form, it was possible to detect their presence in solution, and even to follow the gradual transformation into ketones.

The most striking property of these unsaturated alcohols is their pronounced tendency to combine with free oxygen and form peroxides. Autoxydation has been observed in a number of ethylene derivatives, but it has not been possible, heretofore, to get definite peroxides whose structure could be determined. The peroxides described in this paper are crystalline solids, sufficiently stable for direct analysis and for the determination of molecular weights. The reactions show that they are represented by the general formula

¹ Ber. d. chem. Ges., 25, 1761.

² Ann. Chem. (Liebig), 296, 242. Ber. d. chem. Ges., 32, 650.

Kohler.

They decompose in solution, or at high temperatures, according to the equation :



EXPERIMENTAL PART.

The large quantity of deoxybenzoin needed for the following experiments was made from benzoin by a combination of the methods recently proposed by Sudborough¹ and by Stobbe and Straus.² A solution of 100 grams of benzoin, in 500 grams of glacial acetic acid, was treated with 75 grams of zinc dust and the mixture heated on a water-bath for 24 hours. The undissolved zinc dust was removed by filtration while the liquid was hot, the filtrate poured into water and allowed to stand until the precipitated oil had solidified. The solid was washed with water and digested with 250 cc. of ether. This dissolved all of the deoxybenzoin, but left a considerable quantity of more complex products. After filtration, the ethereal solution was dried over calcium chloride, the ether evaporated and the residue distilled, as recommended by Stobbe and Straus. The yield of pure ketone was 65 to 70 per cent of the calculated amount.

The isomeric ketones were made from deoxybenzoin by the method of Stobbe and Niedenzu,³ but it was found much better to operate at a higher temperature. No addition product with hydrochloric acid is formed when the condensation is carried out at 100°, hence it is possible to avoid the irksome removal of excess of benzaldehyde with bisulphite and to purify the product by distillation under diminished pressure. The procedure was as follows: A moderately rapid current of dry hydrogen chloride was passed, for 2-4 hours, through a mixture of equal weights of benzaldehyde and deoxybenzoin,

¹ J. Chem. Soc., 71, 219.

² Ann. Chem. (Liebig), 319, 163.

³ Ber. d. chem. Ges., 34, 3900.

contained in a Claisen distilling flask that was heated with boiling water. The flask was then connected with a pump, the pale yellow liquid freed from hydrochloric acid and water, and the residue distilled under diminished pressure. The distillate was collected in 3 fractions. The first, collected to 160° (11 mm.) contained almost pure benzaldehyde.

The second, 160° – 230° , solidified in the receiver. It contained, besides small quantities of stilbene and unsaturated ketone, mainly deoxybenzoin, which was easily recovered by distillation and crystallization from alcohol. The remainder of the liquid distilled almost completely between 230° – 260° . The yellow to orange distillate was poured into three times its volume of absolute alcohol and the solid that separated recrystallized from alcohol until free from color. The mixture of the two ketones obtained in this way was easily separated by crystallization from a mixture of ether and ligroin, as recommended by Stobbe and Niedenzu, or from acetone and alcohol as proposed by Klingemann.¹ The yield was good—100 grams of deoxybenzoin gave 96 grams of the mixed ketones and 10 grams of unchanged deoxybenzoin. The composition of the mixture depends upon the length of time employed in the condensation. Thus, 50 grams obtained by heating for 2 hours, contained 28 grams of the high-melting ketone, while the same amount, obtained by heating for 5 hours, contained 43 grams. The relatively large amount of the high-melting ketone obtained in these experiments is due to rearrangement during distillation. When the product, obtained from 100 grams of deoxybenzoin by heating for 2 hours, was separated by crystallization instead of by distillation, it gave 72 grams of the low-melting ketone.

Reactions with Magnesium Compounds.

Stobbe and Niedenzu compared the behavior of the two isomeric ketones with various reagents—bromine, hydrochloric acid, deoxybenzoin—which combine with unsaturated compounds. They found that the reactions took place slowly, were always incomplete and were accompanied by rearrange-

¹ Ann. Chem. (Liebig), 275, 64.

ment; that the high melting ketone combined more readily than its isomer and that both ketones invariably gave the same product. The reactions with organic magnesium compounds proceed rapidly and they are complete, but the products from both ketones are likewise the same. This conclusion was established as follows: Cooled, ethereal solutions, containing 5 grams of the ketones, were added, drop by drop, to similar solutions of ethylmagnesium bromide that were cooled in a freezing mixture. Each drop of the solutions produced a yellow precipitate, which disappeared on shaking. The resulting solutions were decomposed with iced hydrochloric acid, the ethereal layers washed thoroughly with ice-water, then mixed with 50 cc. of alcohol for the purpose of preventing the formation of peroxides and evaporated to crystallization on the water-bath. Each of the ketones gave a mixture of the two stereoisomeric modifications of diphenylvalerophenone that were described in an earlier paper.¹ The total yields were 6.2 grams and 6.3 grams, in place of 6.5 grams calculated. The mixtures were separated by extraction with cold alcohol, in which the high-melting ketone is very sparingly soluble. The product from benzaldehyoxybenzoin gave 5.1 grams of low-melting and 0.8 gram of high-melting ketones, while the product from *iso*-benzaldehyoxybenzoin gave 5.3 grams and 0.7 gram of the substances.

By changing the conditions it was found that the relative amounts of the two products depend solely upon the method of isolation. When the solid ketones were added to boiling solutions and the products isolated as in the first experiment, the relative amounts of stereoisomers obtained were almost the same as before—5 grams of low-melting and 0.9 gram of high-melting in one case and 4.9 grams and 1.0 gram in the other. But when the reactions were carried out in a freezing mixture, as in the first experiment, and the magnesium derivatives poured into water instead of iced hydrochloric acid, the relative quantities were quite different, 3 grams of low-melting to 3.1 grams of high-melting in one case and 2.5 grams to 3.8 grams in the other. In view of these results it seemed prob-

¹ THIS JOURNAL, 35, 399.

able that the two isomeric products had been formed from the same magnesium derivative. To test this view, ethereal solutions of the magnesium derivative were prepared as described in the first experiment and treated, in a freezing mixture, with a cold, dilute solution containing one molecule of benzoyl chloride for each atom of magnesium used in the preparation of the ethylmagnesium bromide. Only one benzoyl derivative was formed and this was obtained in calculated quantity from both ketones.

Triphenylpentenyl Benzoate,

$C_2H_5CH(C_6H_5)C(C_6H_5):C(C_6H_5)OCOC_6H_5$.—The crude product, isolated in the usual way, was purified by crystallization from absolute alcohol. It separated in long needles, melting at 143° . Analysis:

0.1321 gram substance gave 0.4165 gram CO_2 and 0.0747 gram H_2O .

	Calculated for $C_{30}H_{20}O_2$.	Found.
C	86.1	85.91
H	6.2	6.28

The compound is readily soluble in acetone and chloroform, moderately in boiling alcohol, sparingly in cold alcohol and ligroin. It seems to represent the stable modification, as no change took place when it was heated to 150° for 40 hours, nor when a solution in benzene was exposed to sunlight, in the presence of iodine. It is very easy to hydrolyze the substance. A saturated, alcoholic solution was treated with the calculated quantity of aqueous potassium hydroxide and the mixture placed in an ice chest. In the course of an hour the high-melting form of diphenylvalerophenone began to separate and at the end of 5 hours the solution was neutral to litmus. The liquid was then poured on ice, the solid dried and extracted with ligroin. Not a trace of low-melting ketone went into solution. The same product was obtained when the substance was heated to 150° , with concentrated hydrochloric acid, but the result was somewhat different when the ester was boiled with an alcoholic solution of the acid, the product in this case containing nearly 10 per cent of low-melting ketone. With cold,

alcoholic hydrochloric acid a still larger amount, 14 per cent, of this ketone was formed. These results seemed to indicate that the low-melting ketone is the primary product of hydrolysis—the isomer being due to subsequent rearrangement. Parallel tests were therefore made with alcoholic solutions of these two ketones, both in the presence of bases and of acids. It was found that, in the presence of potassium hydroxide, the low-melting ketone passes rapidly and completely into its isomer even in a freezing mixture and that the same change takes place more slowly, but just as completely, in the presence of hydrochloric acid. The high-melting ketone, of course, remained unchanged. The presence of the low-melting ketone in the products of hydrolysis proves, consequently, that this is the primary product of that reaction.

Triphenylpentenylacetate,

$C_2H_5CH(C_6H_5)C(C_6H_5) : C(C_6H_5)OCOCH_3$.—This ester was made and purified like the corresponding benzoate. The same substance was obtained from both unsaturated ketones. It crystallizes in fine needles, melting at 120° , is readily soluble in acetone, chloroform and boiling alcohol and, on hydrolysis, behaves exactly like the corresponding benzoate. Analysis :

0.1221 gram substance gave 0.3761 gram CO_2 and 0.0760 gram H_2O .

	Calculated for $C_{26}H_{24}O_2$.	Found.
C	84.26	84.01
H	6.74	6.91

All the results described up to this point were obtained with each of the unsaturated ketones. As they show conclusively that both ketones invariably give the same products, the subsequent experiments were performed only with one or other, or, frequently, with a mixture of the two substances. The simplest interpretation of these results is as follows: Both of the unsaturated ketones combine with ethylmagnesium bromide to form the same magnesium derivative of triphenylpropenol. From this magnesium derivative acids liberate the corresponding modification of the unsaturated alcohol, while acid chlorides

form its esters. The esters, on hydrolysis, give the same unsaturated alcohol and this, on rearrangement to ketone, gives only the low-melting form of diphenylvalerophenone, which subsequently passes, more or less completely, into its stereoisomer. The evidence in favor of this view, while strong, is not conclusive, because not a single experiment gave only the low-melting ketone. I therefore endeavored to isolate the enol itself.

For this purpose the magnesium derivative, prepared as in previous experiments, was poured on cracked ice that was covered with alcohol-free ether, the basic magnesium salt was dissolved with a freezing mixture of ice and hydrochloric acid and the ethereal layer washed, as quickly as possible, with small quantities of ice water. The moist, ethereal solution was then transferred to a distilling flask immersed in a freezing mixture and the ether evaporated under diminished pressure. The colorless oil that was left was evidently the unsaturated alcohol. It was readily and completely soluble in cold, low-boiling ligroin, in which the isomeric ketones are insoluble, and it reduced an acetone solution of potassium permanganate, which is not attacked by the ketones. All efforts to get the substance in a solid form, in which it might have a moderate degree of stability, failed. When allowed to stand in a freezing mixture it slowly solidifies, but the solid does not reduce permanganate. The composition of this solid, however, fully confirms the interpretation offered above. Forty-five grams, obtained by combining the products of 4 experiments, gave only 0.17 gram of high-melting diphenylbutyrophenone, all of the remainder being the low-melting isomer.

Since the enol could not be isolated in the solid form, it was necessary to find some reagent by which it could be separated from the isomeric ketones. It reduces potassium permanganate, but the process is accompanied by rearrangement and the product bears no simple relation to the original substance. Although unsaturated, the enol does not combine with either bromine or hydrochloric acid and in the presence of traces of these substances it rapidly passes into the isomeric ketones. After many fruitless experiments it was found that the unsaturated

alcohol readily combines with atmospheric oxygen, and that this admirably serves the purpose of a reagent. The procedure is as follows: The moist, ethereal solution of the unsaturated alcohol, prepared as already described, is transferred to a filter flask that is immersed in a freezing mixture. A rapid current of air is drawn through the liquid for several hours, the evaporated ether being replaced from time to time either with more anhydrous ether, or with low-boiling ligroin. If the product is oily it is dissolved in low-boiling ligroin. From this solution the peroxides always separate, on slow evaporation, in a crystalline form.

The oxygen addition product from triphenylpentenol solidified to a hard, colorless cake. This was ground up, washed with small quantities of absolute alcohol to remove adherent moisture, and dissolved in acetone. The first crop of crystals separated in thick needles which, after a second crystallization from the same solvent, melted sharply at 166° and decomposed immediately after melting. The filtrates from these needles contained a second substance that separated slowly, in large, transparent prisms. This was purified by recrystallization from ligroin. It melts at 109° . Analysis of these products showed that they are isomeric, and a molecular weight determination, carried out in boiling acetone, showed that both are monomolecular.

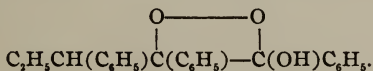
I. 0.1360 gram substance (166°) gave 0.3980 gram CO_2 and 0.0782 gram H_2O .

II. 0.1161 gram substance (110°) gave 0.3388 gram CO_2 and 0.0674 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{22}\text{O}_3$	I.	Found.	II.
C	79.79	79.82		79.59
H	6.36	6.40		6.44

The substances are evidently formed by the addition of a molecule of oxygen either to triphenylpentenol or to the isomeric ketones. Parallel experiments showed that no peroxides are formed when air or oxygen is passed through cooled, ethereal solutions of the ketones, and another set of experiments proved that the product of the reaction with ethylmag-

nesium bromide contains no substance that might act as a catalyst in the autoxydation of the ketones. These experiments were conducted as follows: An ethereal solution, made from 15 grams of deoxybenzoin, was diluted to 240 cc. with absolute ether and divided into 3 equal portions. After adding 5 grams of low-melting ketone to one of these and the same weight of high-melting to another, a current of air was passed through all three. The solution to which no ketone had been added gave 6.3 grams of crude, dry peroxide. The second solution deposited a mixture of low-melting ketone and peroxide. The latter was destroyed with boiling, alcoholic hydrochloric acid and the residue extracted with cold ligroin. This left 4.87 grams of ketone instead of 5 grams originally added. Since the third portion, after similar treatment, left 4.92 grams of ketone, it is evident that the isomeric peroxides are not derived from the ketones but from the unsaturated alcohol. This gives, as the most probable formula,

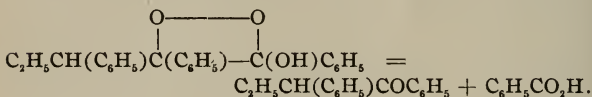


The peroxides from triphenylpentenol are stable substances. They do not give hydrogen peroxide with water, do not liberate iodine from iodides, nor give up oxygen to indigo. When perfectly pure they are not changed by air or direct sunlight, but, in the presence of minute quantities of impurities, they gradually become yellow and ultimately turn into gums. When heated in quantity they decompose with a flash, but without detonation. For the purpose of determining the products of decomposition, 5 grams of each were dropped, in small portions, into flasks heated to 170°, in an oil-bath. The pale-yellow products were dissolved in ether, the solution extracted with aqueous sodium carbonate and the ether evaporated. From the solution in sodium carbonate hydrochloric acid precipitated pure benzoic acid. The ethereal solution, in each case, left an oil which ultimately solidified. The solids, after recrystallization from ligroin, melted at 58°, the same products being obtained from both peroxides. Analysis:

0.1302 gram substance gave 0.4082 gram CO_2 and 0.0855 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{16}\text{O}$.	Found.
C	85.71	85.42
H	7.14	7.22

The composition and melting point indicated ethyldeoxybenzoin. This was confirmed by making the oxime, which melted at 130° . The decomposition by heat is, therefore, similar to that of the ozonides described by Harries.¹ It is represented by the equation :



In solution the same decomposition takes place at much lower temperatures and it is accelerated both by acids and by bases. From a solution in absolute alcohol, which contained one equivalent of potassium hydroxide for one of peroxide, potassium benzoate began to separate, at the ordinary temperature, in less than half an hour and at the end of 3 hours the liquid was neutral.

Owing to the ease with which the peroxides decompose it was not possible to make an acetyl derivative either with acetyl chloride or acetic anhydride, but the presence of hydroxyl was easily established with ethylmagnesium bromide. A solution of the reagent was slowly siphoned into an ethereal solution containing excess of the peroxide (166°). The reaction was accompanied by a steady evolution of gas, and almost the entire amount of peroxide was recovered when the product was decomposed with ice.

The formula proposed accounts for these reactions and also for the formation of two isomeric peroxides. It contains 3 unequal, asymmetric carbon atoms, but since the reaction is accompanied by ring formation, only *cis*-addition of oxygen is to be expected. With an inactive substance containing one asym-

¹ Ann. Chem. (Liebig), 343, 311.

metric carbon atom this process would result in two racemic modifications.

With the help of these peroxides it was possible to make a rough estimate of the rate at which triphenylpentenol passes into the isomeric ketones. An ethereal solution, containing approximately 25 grams of the alcohol, was diluted to 500 cc. and placed in an ice-chest. At intervals, 100 cc. of the solution were drawn off with a pipette and evaporated in a current of air. The solid residue was boiled with alcoholic hydrochloric acid, to destroy any peroxide formed, and the alcohol evaporated to dryness. By extracting the residue with cold methyl alcohol, ethyldeoxybenzoin could be removed without losing more than a trace of diphenylvalerophenone (170°). The first trial, made immediately after preparing the solution, gave only 0.3 gram of ketone, showing that almost no rearrangement had taken place when the magnesium compound was decomposed with water. The remaining tests gave the following results: After 10 hours, 2.1 grams of ketone; 24 hours, 4.4 grams; 30 hours, 5.4 grams; 50 hours, 5.25 grams. These numbers represent only very rough approximations; it was not possible to duplicate experiments and get the same results. In one experiment, in which the ethereal solution had been made with the greatest care, no peroxide could be detected after the lapse of 8 hours.

Tetraphenylpropenol, $(C_6H_5)_2CHC(C_6H_5):C(OH)C_6H_5$.—When benzaldeoxybenzoin is treated with phenylmagnesium bromide, the product, isolated in the usual way, is triphenylpropiophenone, which has been described in a previous paper.¹ By bringing the substances together in ligroin, and treating the product as described under the reaction with ethylmagnesium bromide, it was possible to get the intermediate, unsaturated alcohol in a solid form. It separated from ligroin in colorless needles, readily soluble in alcohol and ether, sparingly in ligroin. The melting point observed depends upon the mode of heating, because the substance passes into the ketone below the melting-point. The true melting point probably lies between 95° and 100°, as was found by dipping capillary tubes containing the

¹ THIS JOURNAL, 34, 568.

substance into water at different temperatures. The enol is so sensitive to oxygen that all operations had to be carried out in nitrogen or carbon dioxide. As it rapidly passes into triphenylpropiophenone on heating, it seemed useless to undertake an analysis.

Tetraphenylpropenolperoxide,

$$\begin{array}{c} \text{O} \text{---} \text{O} \\ | \quad | \\ (\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5)\text{C}(\text{OH})\text{C}_6\text{H}_5 \end{array}$$

—The crude product, obtained by passing air through a solution of the alcohol, was purified by crystallization from acetone and ligroin. Analysis :

0.1163 gram substance gave 0.3509 gram CO_2 and 0.0606 gram H_2O .

	Calculated for $\text{C}_{27}\text{H}_{22}\text{O}_3$.	Found.
C	82.21	82.29
H	5.58	5.79

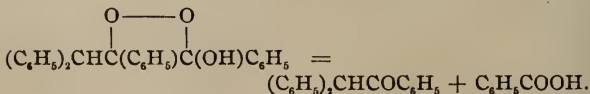
The peroxide crystallizes in small, lustrous prisms that melt at 127° . It is readily soluble in alcohol, ether, chloroform and acetone ; sparingly soluble in ligroin. When heated by itself, or with hydrochloric acid in alcoholic solution, it decomposes into benzoic acid and a substance melting at 139° – 140° . Analysis :

I. 0.1386 gram substance gave 0.4473 gram CO_2 and 0.0742 gram H_2O .

II. 0.1516 gram substance gave 0.4900 gram CO_2 and 0.0808 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{16}\text{O}$.	I.	Found.	II.
C	88.23	88.02		88.14
H	5.88	5.94		5.92

By analogy with the behavior of the peroxides previously described the substance would be expected to give diphenylacetophenone, according to the equation :



A compound of this composition was discovered by Delacre,¹ and subsequently studied with care by Gardeur² and by Biltz.³ Gardeur agreed with Delacre and believed that the substance is a ketone, while Biltz regards it as the isomeric unsaturated alcohol. The principal reasons for the latter view are : The instability of the substance in the presence of alcoholic potassium hydroxide, which decomposes it into diphenyl methane and benzoic acid ; the ease with which the hydrogen is replaced by bromine ; the inability of all investigators to get an oxime ; and the fact that Biltz obtained an acetyl derivative by boiling the substance with sodium acetate and acetic anhydride, and the corresponding benzoyl derivative by boiling it with benzoyl chloride and pyridine.

My product is evidently identical with the substance studied by Biltz and by Gardeur. It has the same melting point, gives the same products with alcoholic potassium hydroxide, and an acetyl derivative, melting at 105°, when treated as directed by Biltz. It differs markedly from the enolic compounds considered in this paper, being perfectly stable and incapable of combining with free oxygen. Biltz's view, therefore, seemed open to doubt, the more so because the strongest evidence for the enol formula offered, the formation of acyl derivatives, is invalidated by the more recent discovery that even ketones may give such derivatives when heated with acid chlorides and pyridine.⁴

The most conclusive method for deciding between the two formulas is to study the behavior of the substance towards Grignard's reagent, because it has been shown that substances like acetoacetic ester decompose the reagent like hydroxyl compounds. It was found that no gas is evolved when the substance in question was added to ethylmagnesium bromide. The product of the reaction was a solid, which was purified by crystallization from methyl alcohol.⁵ It crystallizes in needles, melting at 91°, and is readily soluble in organic solvents.

Analysis:

¹ Bull. Soc. Chim., [3], 13, 859.

² Centrabl., 1897, II., 660.

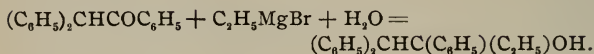
³ Ber. d. chem. Ges., 32, 650.

⁴ Lees : J. Chem. Soc., 190, 3 ; 84, 145. Claisen : Ber. d. chem. Ges., 36, 3674.

0.1142 gram substance gave 0.3655 gram CO_2 and 0.0755 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{22}\text{O}$.	Found.
C	87.41	87.27
H	7.28	7.34

The substance is evidently an alcohol, formed according to the equation:



This conclusion was confirmed by treatment with ethylmagnesium bromide.

Diphenylacetophenone Oxime $(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5) : \text{NOH}$.—Although Delacre and Biltz failed to get an oxime by boiling the ketone with hydroxylamine hydrochloride, it seemed possible that the substance might be obtained in alkaline solution. Under these conditions a large part of the ketone is destroyed, but the first experiment, in which an alcoholic solution, containing 1 molecule of ketone to 3 molecules of hydroxylamine hydrochloride and 9 molecules of potassium hydroxide, was boiled for an hour, yielded a small quantity of nitrogenous product melting at 180° . The process was repeated many times without getting a trace of this substance, but at last an experiment carried out in the same way gave 1.5 grams, from 5 grams of ketone. The product was purified by recrystallization from acetone, from which it separates in plates. Analysis:

I. 0.0542 gram substance gave 0.2578 gram CO_2 and 0.0463 gram H_2O .

II. 0.4600 gram substance gave 20.8 cc. N at 18° and 754 mm.

	Calculated for $(\text{C}_{20}\text{H}_{17}\text{OH}\cdot\text{N})$	I.	Found.	II.
C	83.62	83.41		..
H	6.06	6.01		..
N	4.87	..		5.12

The oxime melts at 182° . It is readily soluble in acetone, sparingly in alcohol. Dilute acids and boiling water quickly

hydrolyze it, the sole organic product being triphenylpropio-phenone.

Bromtriphenylpropio-phenone, $(\text{C}_6\text{H}_5)_2\text{CHCBr}(\text{C}_6\text{H}_5)\text{COC}_6\text{H}_5$.—This substance was obtained by treating the magnesium derivative of tetraphenylpropenol with bromine. It was purified by crystallization from a mixture of chloroform and alcohol, from which it separates slowly in large prisms, melting at 124° . It is readily soluble in chloroform, moderately in acetone, very sparingly in alcohol.

0.1515 gram substance gave 0.4088 gram CO_2 and 0.0667 gram H_2O .

	Calculated for $\text{C}_{27}\text{H}_{21}\text{OBr}$.	Found.
C	73.47	73.58
H	4.76	4.88

It is easy to eliminate hydrobromic acid from this substance and thus get a new unsaturated ketone. This is still under investigation.

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BRYN MAWR COLLEGE,
May, 1906.

VARIABLE SENSITIVENESS IN COLORIMETRY. II.¹

BY DAVID W. HORN AND SUE A. BLAKE.

In a previous contribution² from this laboratory, it was shown that, at certain definite concentrations, the comparisons in the colorimetric determination of chromium can be made with greater ease and accuracy than at other concentrations. An appreciable difference in color in dilute solutions of potassium chromate and of chromium sulphate is produced, in some cases, by a much smaller weight of chromium than in others. The figures did not show any simple relation, however, between the concentrations of the solutions and the minimum weights

¹ Read in abstract before the Philadelphia Section, Amer. Chem. Soc., March 17, 1906.

² THIS JOURNAL, 35, 253.

of chromium necessary to produce appreciable changes in color.

In the present paper the results for potassium chromate, reduced to values suitable for graphic representation, are presented again and discussed along with the results of a study of a second case, that of copper sulphate. Copper sulphate was selected for this study because the color of its solutions is quite different from that of those previously studied, and is due to a kathion.

The experimental results are given in the following tables :

Table I.—Solutions of Potassium Chromate.

Number of experiment.	V. Concentration stated as liters that contain one gram atom of Cr.	Milligrams of Cr producing a just perceptible difference in color in 50 cc.	S. Sensitiveness: reciprocals of values found in column 3.	$\frac{\sqrt{V}}{25}$.	$\frac{S}{150}$.
				5.	6.
1.	250.0	3.979	0.25	0.63	0.002
2	500.0	0.784	1.28	0.90	0.009
3	666.6	0.386	2.59	1.03	0.017
4	1000.0	0.184	5.43	1.26	0.036
5	2000.0	0.074	13.51	1.79	0.090
6	3600.0	0.007	142.86	2.40	0.952
7	4000.0	0.002	500.00	2.53	3.33
8	8000.0	0.001	1000.00	3.58	6.66
9	9900.0	0.005	200.00	3.98	1.33
10	10666.6	0.008	125.00	4.13	0.83
11	16000.0	0.011	90.90	5.06	0.61
12	17700.0	0.003	333.33	5.33	2.22
13	32000.0	0.0007	1428.60	7.16	9.52
14	110000.0	0.011	90.90	13.27	0.61
15	150000.0	0.008	125.00	15.50	0.83
16	200000.0 not distinguishable from distilled water.				

Table II.—Solutions of Copper Sulphate.

Number of experiment.	V. Concentration stated as liters that contain one gram atom of Cu.	Milligrams of Cu producing a just perceptible difference in color in 50 cc.	S. Sensitiveness: reciprocals of values found in column 3.	$\frac{\sqrt{V}}{1.75}$	$S \times 7.7$
1.	2.	3.	4.	5.	6.
1	1.64	154.51	0.006	0.71	0.05
2	3.28	77.25	0.013	1.00	0.10
3	24.42	12.36	0.081	2.78	0.62
4	37.99	8.03	0.124	3.57	0.95
5	45.72	5.41	0.185	3.85	1.42
6	52.61	6.18	0.162	4.14	1.25
7	55.64	5.79	0.173	4.28	1.33
8	68.61	3.86	0.259	4.71	2.00
9	69.43	4.63	0.216	4.78	1.66
10	82.28	3.86	0.259	5.21	2.00
11	85.72	3.86	0.259	5.28	2.00
12	91.51	3.86	0.259	5.49	2.00
13	102.91	3.09	0.323	5.78	2.49
14	128.74	2.32	0.431	6.49	3.32
15	164.77	1.16	0.862	7.35	6.64
16	187.06	0.77	1.299	7.85	9.96
17	329.53	1.74	0.575	10.42	5.97
18	748.24	1.93	0.518	15.64	3.99
19	4892.30 just distinguishable from distilled water.				

The values in columns 5 and 6 in Tables I. and II. are represented graphically in Figs. I. and II., respectively. Distances on the horizontal axis are proportional to the square roots of the concentrations, and distances on the vertical axis to the sensitiveness. The *square roots* of concentrations are used to make the graphs less extensive. Solutions of potassium chromate, of concentrations corresponding to the maxima and minima in Fig. I., were examined with a spectrometer; as was anticipated, no measurable differences in the refractive indices were found.

When the two graphs are compared the resemblance between that for copper sulphate solutions and the first part of that for potassium chromate solutions is apparent. This agreement in

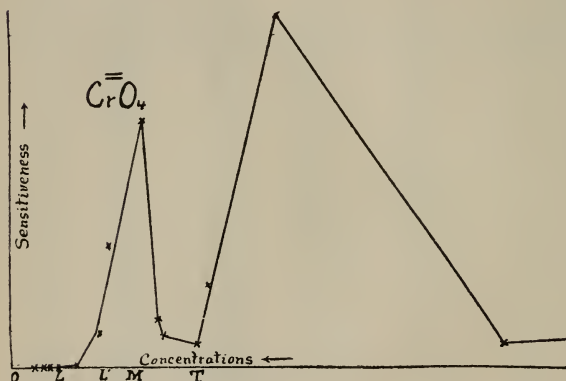


Fig. I.

form was noticed early in the work and suggested that, in both cases, we had to deal with the same phenomena. Experiments 19, Table I., and 15 and 16, Table II., show that the tinctorial power of Cu^{++} is only about one-thirtieth that of $\text{CrO}_4^{=}$; from this it would be expected that the same phenomena would appear on different scales in the two cases. In the experiments with K_2CrO_4 the range of concentrations was N/250 to N/150000, whereas with CuSO_4 it was only N/1.6 to N/748.

The results in Table II., when amplified as in the following table, Table III., show :

1. The ratio between the amount of copper that just suffices

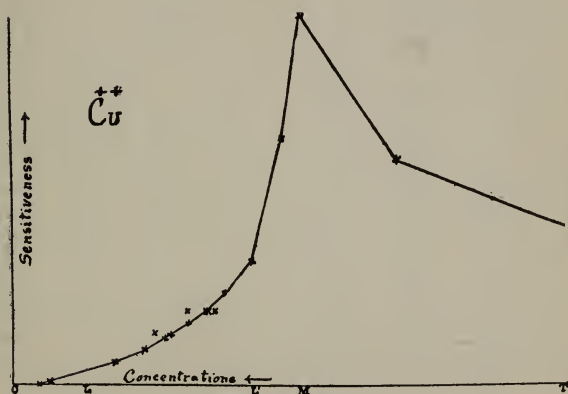


Fig. II.

to produce an appreciable difference in color in 50 cc. of each solution and the total amount of copper present in 50 cc. of the solution at the different concentrations studied, a relation represented in the table by Δ/β' .

2. The ratio between the total amounts of copper in two 50 cc. tubes containing solutions that exhibit the minimum perceptible difference in color, a relation represented in the table by β/β' .

In Table III. the experiments are numbered and given in the same order as in Table II.

Table III.—Copper Sulphate Solutions.

1. Number of experi- ment.	2. Milligrams Cu: total in 50 cc. of β . solution.	3. Milligrams Cu pro- ducing just percep- tible difference in color in 50 cc. Δ .	4. $\beta + \Delta = \beta'$.	5. Δ/β' .	6. Variation from mean in experi- ments 3-14, inclu- sive.	7. β/β' .	8. Variation from mean in experi- ments 1-14, inclu- sive.
1	1931.3	154.51	2085.81	0.07		0.93	+0.01
2	965.6	77.25	1042.85	0.07		0.93	+0.01
3	130.2	12.36	142.56	0.09	0.00	0.92	0.00
4	83.7	8.03	91.73	0.09	0.00	0.91	—0.01
5	69.5	5.41	74.91	0.09	0.00	0.93	+0.01
6	60.5	6.18	66.68	0.09	0.00	0.91	—0.01
7	57.2	5.79	62.99	0.09	0.00	0.91	—0.01
8	46.4	3.86	50.26	0.08	—0.01	0.93	+0.01
9	45.8	4.63	50.43	0.09	0.00	0.91	—0.01
10	38.7	3.86	42.56	0.09	0.00	0.91	—0.01
11	37.1	3.86	40.96	0.09	0.00	0.91	—0.01
12	34.8	3.86	38.66	0.10	+0.01	0.90	—0.02
13	30.9	3.09	33.99	0.09	0.00	0.91	—0.01
14	24.7	2.32	27.02	0.09	0.00	0.92	0.00
15	19.3	1.16	20.46	0.06		0.94	
16	17.0	0.77	17.77	0.04		0.96	
17	9.7	1.74	11.44	0.15		0.85	
18	4.3	1.93	6.23	0.31		0.69	

Through a wide range of concentration the values of Δ/β' and β/β' are approximately constant. The variations from the average values, columns 6 and 8, probably represent necessary errors in our experiments. If we had maintained the same conditions as to illumination and use of the eyes prior to each experiment, the errors might have been reduced. Our intention, throughout, was to work under conditions that generally prevail in the laboratory practice of colorimetric analysis. That the errors have very little effect on the form of the graph is readily seen from the relative positions of the points and line in Figure II.

Discussion of Results.

The agreement in form in the curves that are the first parts of the graphs show that the relations set forth by the curves are the same in both cases. For the special case of copper this relation may be stated in several ways, depending on what part of the results we emphasize.

1. If we consider the ratio Δ/β' the following is true:

The amount of copper that will produce, at different concentrations, a difference in color that can just be distinguished is not a constant weight, but is a constant fraction of the total weight of copper present. Exceptions occur when the solutions are too dilute or too concentrated.

2. If we consider the ratio β/β' , the following is true:

Whenever the difference in color between copper solutions is estimated as just perceptible, the ratio between the two quantities of copper in the solutions compared is always the same. That is,

$$y' - y = k \beta' / \beta$$

where y' and y represent two sensations that are just distinguishable, corresponding to two weights of copper β' and β .

3. If we consider the variations of the sensitiveness, S , column 4, Table II, with the total copper, the following is true:

$$\beta S = \beta_1 S_1 = \beta_2 S_2 = \beta_n S_n = \text{constant.}$$

The product of the sensitiveness into the total copper is a constant; or, in other words, *the sensitiveness varies inversely as the total copper.*

We are aware of no changes that occur with dilution, in solutions such as we have worked with, that account for the variations in sensitiveness.

Application to Colorimetric Analysis.

There are reasons for believing that the relation which holds in the two cases studied is a general relation throughout the whole field of colorimetry. The actual effect of the variation of sensitiveness with concentration upon the results obtained in any colorimetric analysis may, then, be stated in a general way; exact statements cannot be made until each colorimetric

method has been examined. This effect would, presumably, be most significant in the field where colorimetry finds its proper application,—that is, where minute amounts of substances must be determined quantitatively, as in water analysis.

In general, the following statements are true:

1. Every colorimetric method possesses at least one maximum of sensitiveness.

At concentrations between L and L' in the graphs Figs. I and II, the relation

$$\beta S = \beta_n S_n$$

holds, and the curve for sensitiveness is a rectangular hyperbola. As dilution progresses a limit L' is reached where this relation ceases to hold. That this must be true is clear, for otherwise the sensitiveness could become *infinitely* great. That it does not do this is evidenced by Experiments 15 and 16 Table I, and 19 Table II. They show that a point is reached by dilution where the solution no longer *appears* colored, although it still contains colored solute.

At or beyond the point where the relation

$$\beta S = \beta_n S_n$$

ceases to hold, the sensitiveness suddenly acquires much lower values, as can be seen from Tables I and II, column 4, or from the two graphs. The corresponding sudden change in direction, or break in the curve marks the maximum of sensitiveness.

2. Solutions may be too concentrated for accurate colorimetric analysis. These correspond to concentrations between the origin O , and L , a limit above which the solutions are too deeply colored. Our results for Δ/β' show where L is located, and this limit has, in most cases, been discovered by experience, as is indicated by the general practice of avoiding the use of deeply colored solutions.

3. As long as the analyst works at concentrations between the limits L and L' , it is a matter of indifference what concentration he may select for work. The percentage error will be the same in all cases. This is probably why the relations we

have pointed out have hitherto been overlooked; usually the analyst has by accident selected concentrations that lie between the limits L and L' .

That the percentage error is always the same at concentrations between these limits L and L' is readily seen from the following examples. In these we assume all the concentrations discussed to lie between L and L' , and we assume the value of the fraction Δ/β' to be 0.1. The whole specimen for analysis contains 1 gram of colored substance, and all of it is brought into solution.

Example (a).

The specimen is dissolved and the solution diluted to 500 cc. The comparisons are made in 50 cc. Nessler cylinders. The experimental error may then be 0.1 of 50/500 of 1 gram, or 0.01 gram in 50 cc.

In calculating the whole amount of colored substance found by this analysis, the error will be multiplied by 10, or will amount to 0.1 gram in the whole 500 cc.; that is, to 0.1 gram in the whole 1 gram; or, to 10 per cent.

Example (b).

The total volume of the solution of the specimen is 50 cc. The error then may be 0.1 of 1 gram or 0.1 gram in 50 cc.; that is, 0.1 gram in the whole 1 gram, or 10 per cent.

Example (c).

The total volume of the solution of the specimen is 2 liters. The error then may be 0.1 of 50/2000 of 1 gram or 0.0025 gram in 50 cc.

In calculating the whole amount of colored substance found by the analysis, this error will be multiplied 40 times, and will amount to 0.1 gram in whole 2 liters; that is, to 0.1 gram in whole 1 gram; or, to 10 per cent.

4. There is an advantage in colorimetric analyses in working between the limits L' and M , that is, at concentrations lying near that of maximum sensitiveness.

This can be illustrated by the case of copper. Suppose, for simplicity, that the whole amount of specimen dissolved contains 1 gram atom, 63.6 grams of copper.

In one case suppose this material is dissolved in 50 liters.

One cylinder will then contain 50/50000 of 63.6 grams, or 0.0636 gram of copper, and the error under consideration may amount to 0.09×0.0636 gram, or 0.00572 gram in 50 cc. This is 5.72 grams in 50 liters, containing all the copper, or 8.9 per cent error.

In a second case suppose the same amount of material is dissolved in 187 liters.

One cylinder will contain 50/187000 of 63.6 grams, or 0.017 gram copper, and the error may amount to 0.04×0.017 gram, or 0.000681 gram in 50 cc. This is 2.54 grams in 187 liters containing all the copper, or 4.0 per cent.

The percentage error has been reduced by more than half, by working near the concentration of maximum sensitiveness, instead of working at some concentration within the limits L, L' .

5. Solutions may be too dilute for accurate colorimetric work. It is scarcely necessary to do more than call attention to the values of the fraction Δ/β' in Experiments 17 and 18, Table III. They are 0.15 and 0.31 instead of the value 0.09 that holds between the limits L, L' , and instead of 0.04 that holds at the maximum of sensitiveness. The percentage error corresponding to the fractions 0.15 and 0.31 are about 15.2 per cent and 31.3 per cent, respectively.

Method of Experiment.

The values for the sensitiveness have been obtained by a more direct method in this case than in that of solutions of CrO_4 . In applying this method in any case, the following procedure is adopted:

1. Make a rough approximation, by the method of comparison and dilution usual in colorimetry, to the limiting amount of colored solute producing a sensible difference in color at some selected concentration. Let us suppose that by this method it is found that 24 cc. of a standard colored solution "S," when put into a 50 cc. Nessler cylinder with 26 cc. of water, gives a solution that can be distinguished with difficulty from one containing 25 cc. of "S" and 25 cc. of water. The difficulty in the distinction is so great as to make it doubtful.

2. The next step is to decide whether or not 1 cc. of "S" does produce a perceptible difference in 50 cc. of the above solutions. To this end prepare a series of tubes marked, let us say, J, K, L, M, N, O and P, respectively, and introduce into them the following volumes of "S" and of water:

	J.	K.	L.	M.	N.	O.	P.
Volume of "S"	28	27	26	25	24	23	22
Volume of water	22	23	24	25	26	27	28

After the contents of the cylinders have been *thoroughly* mixed and each cylinder has been slipped into a black paper jacket, mix the cylinders until their identities, as indicated previously by their relative positions, are lost, and then arrange them in the order of their apparent intensities of color. After they had been thus arranged, if they are found, always to be arranged in the alphabetical order, three to ten times, it is obvious that 1 cc. of "S" produces in 50 cc. of solution a difference in color that is unmistakably perceptible. The concentration to which this result applies is the average concentration of the series of solutions, that is, the concentration of solution in tube M.

3. In the first experiment by 2, it often happens that the tubes at one end of the series are arranged by color in the proper order, while those at the other end are confused. Thus, M, N, O, P may be correctly arranged, while J, K and L are confused. This indicates that the colors of the solutions in J, K and L are too deep for 1 cc. of "S" to produce an appreciable change in them. In such a case put J, K and L aside and introduce into the series Q, R and S, containing

	Q.	R.	S.
Volume of "S"	21	20	19
" " water	29	30	31

Mix the tubes and arrange according to intensity of color. The ability to arrange the series repeatedly in the alphabetical order indicates that the quantity, 1 cc. of "S," is sufficient to produce a perceptible difference at the concentration of solution in the middle tube of the new series, that is, in P.

In other cases, when the lower tubes of a series are sometimes confused, the reverse procedure is adopted.

The process of substituting tubes and thus lowering or raising the average concentration, while retaining the same difference in concentration, is continued, if necessary, until a series of tubes is obtained showing unmistakable differences in color.

4. In other cases it may be recognized, in the first approximation, that the ease in making the distinctions is relatively great. In these circumstances, select L, M, N from the series and add to them 4 additional tubes to form the following new series :

	KL.	L.	LM.	M.	MN.	N.	NO.
Volume of "S"	26.5	26	25.5	25	24.5	24	23.5
" " water	23.5	24	24.5	25	25.5	26	26.5

If this series is arranged by color readily in its alphabetical order, select from it LM, M, MN and add new tubes to form the following series :

	LLM.	LM.	LMM.	M.	MMN.	MN.	MNO.
Volume of "S"	25.75	25.50	25.25	25	24.75	24.50	24.25
" " water	24.25	24.50	24.75	25	25.25	25.50	25.75

By following (3) and (4), separately or combined, as occasion demands, it is possible to arrive directly at the difference in weight of colored solute just detectable at an average concentration that is known.

A Possible Interpretation of the Results.

Our results are strongly suggestive of the psychophysical law known as Weber's Law. One assumption must be made in order that our results may be compared with the law, it is that the strength of the stimulus producing the sensation of blueness, caused by light that has passed through a tube of solution to the eye, is directly proportional to the quantity of copper contained in the solution. This assumption seems to us almost axiomatic.

With respect to the first relation, represented by

$$\frac{\Delta}{\beta'} = \text{constant},$$

we have the two following statements for comparison :

The amount of copper that produces, at different concentrations, a difference in color that can just be distinguished is a constant fraction of the total weight of copper present (*vide* p. 201).

The increment in stimulus that produces a just perceptible difference in sensation is always the same fraction of the total stimulus (Weber's Law).

With respect to the second relation, represented by

$$y' - y = k\beta'/\beta,$$

we have for comparison these two statements :

Whenever the difference in color between two copper solutions is just perceptible, the ratio between the two quantities of copper in the solutions is always the same (*vide* p. 201).

A difference between any two sensations will be estimated as equally perceptible if the relation between the stimuli is the same (Weber's Law).

On the assumption indicated, the statements in each pair are identical.

Weber's Law applies very closely to our results within the limits of concentration L and L' . From the limit L' to the point near T , where the sensation of color disappears, the law is not valid.

As our results are independent of Weber's Law, we have no intention of entering the discussion of its merits. Our main interest in the law arises from the fact that if, as stated by certain authorities, von Helmholtz¹ for example, it holds for the sensitiveness of the eye for mean degrees of intensity of sensation, there can be no doubt that the relation we have found in

¹ "Popular Lectures" translated by Atkinson, Series 2, pp. 101-6. Compare von Helmholtz: "Handb. der Physiologischen Optik," 2 ed., 1896, 387, 683. Fechner, G. T.: "Elemente der Psychophysik," 2 ed., 1889, II., 1. Wundt, W.: "Grundzüge der Physiologischen Psychologie," 5 ed., 1902, I., 493. Köhler: A.: "Ueber d. hauptsächlichsten Versuche eine math. Formulierung des p. p. Gesetzes von Weber," Philosophische Studien, 1886, 3, 572.

the colorimetry of $\text{CrO}_4^{=}$ and Cu^{++} is a perfectly general one throughout colorimetry.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
May, 1906.

ON THE PREPARATION OF THE CYANAMIDES.

BY RALPH H. MCKEE.

In the study of another problem, it became necessary to prepare the mono- and dialkyl cyanamides in quantity. Examination of the literature brought to light a number of methods, but each is subject to criticism, being either troublesome and tedious in application,¹ or using, as one of the starting materials, a substance difficult to prepare and not on the market.² The yields also are unsatisfactory; in general the amines are used as the starting material and considerably less than one-half is transformed into the corresponding cyanamides.³

A general method has now been found by which the amines can be changed quickly and easily, nearly molecule for molecule, into the corresponding cyanamides. It is the purpose of the present paper to discuss this general method and the modifications necessary in a few special cases. The applicability of the method to the transformation into cyanamides of acid amides and of amines containing ring groupings will also be pointed out.

The preparation of the dialkylcyanamides may be typified by the preparation of dipropylcyanamide:

Dipropylcyanamide, $(\text{C}_3\text{H}_7)_2\text{NCN}$.—Twenty and two-tenths grams (1 mol.) of dipropylamine were added to a solution of 69 grams (4.5 mol.) of potassium cyanide, in 200 cc. water, and to the whole, kept below 15° , there was added, in about 1 cc. portions, a solution of 11 cc. (1.1 mol.) of bromine, in 60 cc.

¹ Cahours und Cloez: *Ann. Chem. (Liebig)*, **90**, 95 (1854). Chancel: *Compt. rend.*, **116**, 329 (1893). Berg: *Ann. de Chimie* (7), **3**, 352 (1894). Wallach: *Ber. d. chem. Ges.*, **32**, 1873 (1899).

² Hofmann: *Ber. d. chem. Ges.*, **2**, 602 (1869); **3**, 264 (1870); **18**, 2784 (1885). Fileti und Schiff: *Ibid.*, **10**, 428 (1877). Braun: *Ibid.*, **33**, 1451 (1900). Braun und Röver: *Ibid.*, **36**, 1196 (1903).

³ Erlenmeyer: *Ibid.*, **14**, 1868 (1881). Kaess und Gruszkiewicz: *Ibid.*, **35**, 3598 (1902).

of low boiling ligroin. During the addition of the bromine solution the flask was shaken so that the dipropylamine hydrobromide formed might be decomposed by the potassium cyanide solution and the dipropylamine set free to be further acted upon by the bromine and potassium cyanide. The ligroin solution was separated from the aqueous liquid, washed with dilute sodium hydroxide, dried with calcium chloride, the ligroin distilled off and the oil remaining in the flask fractionated *in vacuo*. The yield was 23.5 grams, boiling exactly at 95° (11 mm.) This is over 93 per cent of the theory. The total time consumed, including 20 minutes' drying of the ligroin solution, was just 2 hours.

It is best to carry out the operation in a hood, as there is some hydrocyanic acid set free during the addition of the bromine solution and some during the removal of the solvent by distillation, the washing with sodium hydroxide failing to remove all the dissolved gas.

By the preparation¹ of methyl dipropylisourea from it the identification of the oil was made complete.

Asymmetrical Methyldipropylisourea, (Methyl Imidodipropylcarbamate), $(C_3H_7)_2NC(:NH)OCH_3$.—A methyl alcoholic solution of dipropylcyanamide (1 mol.) was treated with a methyl alcoholic solution of sodium methylate (1.1 mol.), the whole heated to 65° for 1.5 hour, the cooled solution made acid with hydrochloric acid and allowed to stand until the small amount of isonitrile, formed as a by-product, had been decomposed. This solution was extracted with ether, to remove any unchanged dipropylcyanamide, and then made alkaline with strong alkali and the separated isourea ether taken up with ether. The ether solution was washed with water, dried with anhydrous sodium sulphate, the ether distilled off and the remaining oil fractioned *in vacuo*. Yield 80 per cent of the theory. Boiling point 98° (19 mm.) and 203° (748 mm.). Density at 22° , referred to water at 4° (Westphal) 0.9103. Methyldipropylisourea is much more soluble in cold than in warm water. An approximate determination of its solubility gave 3.5 parts at 15° , and 1.5 parts at 50° , in 100 parts of water.

¹ Cf. McKee: THIS JOURNAL, 26, 236 (1901).

Analysis (Kjeldahl-Gunning). Found, 17.82 per cent; calculated for $C_8H_{18}N_2O$, 17.74 per cent nitrogen.

This is the first known oxygen ether of the ureas having two aliphatic groups attached to nitrogen. It is also the first isourea to boil at atmospheric pressure without decomposition; even the mother substance, methylisourea, $NH_2C(:NH)OCH_3$, from which the present isourea is derived, decomposes on attempting to distil it under atmospheric pressure.¹

Diisobutylcyanamide, $(C_4H_9)_2NCN$, was prepared in the same manner as dipropylcyanamide. The yield was 83 per cent, boiling at 123° (25 mm.).

Diisoamylcyanamide, $(C_5H_{11})_2NCN$, was obtained by the same method in a yield of over 92 per cent of the theory. Diisoamylamine hydrobromide is soluble to the extent of less than 3 parts in 100 parts of water at 15° , and is practically insoluble in ligroin. In order to liberate the amine from its slightly soluble hydrobromide, by the action of the weakly alkaline potassium cyanide solution, it is necessary to shake long and vigorously, thereby doubling the time required for the preparation of the cyanamide. Diisoamylcyanamide boils at 134° (14 mm.).

Diethylcyanamide, $(C_2H_5)_2NCN$.—Ethyl acetate is to be preferred to ligroin as a solvent when the molecular weight of the desired substance is small, or when the amine used, or cyanamide formed is but slightly soluble in ligroin. The reaction can be the easier controlled if the amine is diluted with several times its volume of ethyl acetate before adding the ethyl acetate solution of bromine.

Using a temperature of about 5° during the addition of the bromine solution, diethylcyanamide, boiling at 188° – 189° (748 mm.), was obtained in good yield. Its identification was made complete by the formation from it of methyldiethylisourea.

Methyl(asym)diethylisourea (*Methyl Imidodiethylcarbamate*), $(C_2H_5)_2NC(:NH)OCH_3$, was prepared by the same method as the methyldipropylisourea. It boils at 171° – 172° (745 mm.). It distills with water, benzene and even ether vapor. Methyl-diethylisourea is a strong monacid base and may be titrated

¹ McKee: THIS JOURNAL, 26, 248 (1901).

with hydrochloric acid. Using 0.1 N hydrochloric acid and methyl orange, 0.4412 gram required 33.87 cc. ; calculated for $C_2H_4N_2O$, 33.88 cc.

Dimethylcyanamide, $(CH_3)_2NCN$, was prepared in the same way as the corresponding ethyl compound, but the yield was very small. The low yield was found to be due to the fact that the cyanamide formed is much more soluble in water¹ than in ethyl acetate. By carrying out the preparation in the presence of but a trace of water, a yield of over 50 per cent of the pure dimethylcyanamide was obtained.

To an ethyl acetate solution of dimethylamine (1 mol.) a few drops of water were added, then powdered potassium cyanide (4 mol.) and an ethyl acetate solution of bromine (1.1 mol.) was run in slowly and with continued shaking. The temperature was 10°–15°. The solution was filtered from the solid, dried, the solvent distilled off and the oil fractioned. The pure substance boils at 98° (104 mm.) and at 164° (740 mm.).

Methylcyanamide, CH_3NHCN , was prepared in the same way as dimethylcyanamide, except that care was taken to prevent polymerization to the melamine, by keeping the temperature below 0° during the addition of the bromine solution. By using a partial vacuum the ethyl acetate was distilled off at a temperature below 40°. From the crude methylcyanamide remaining after distilling off the ethyl acetate, fairly pure methylcyanamide may be obtained by extracting with a little absolute ether and evaporating the ether extract. The yield is poor, 30 per cent, but apparently it is as good as by the other methods² given in the literature.

The ethyl acetate solution of methylamine must be used at once after its preparation, as otherwise there is considerable loss due to the interaction of the amine and solvent. A solution which showed 9.5 per cent of methylamine by titration, after standing over night, at room temperature, contained only

¹ Cf. Braun und Röver : *Loc. cit.*

² Cahours und Cloez : *Loc. cit.* Cf. Erlenmeyer : *Loc. cit.* Kaess und Gruszkiewicz : *Loc. cit.* Hofmann : *Ber. d. chem. Ges.*, 3, 264 (1870).

1 per cent of methylamine which had not reacted with the solvent.

The methylcyanamide was identified by its change, on heating, to isotrimethylmelamine, which, after washing with water and drying on a clay plate, melted at 123° – 124° when quickly heated, then solidified and finally remelted 50° higher. Freund und Schwarz¹ give this melamine as having the double melting point of 123° – 124° and 179° .

Ethylcyanamide, C_2H_5NHCN , was prepared from ethylamine in the same way as methylcyanamide from methylamine, but the yield, 71 per cent, was much better than with the methyl compound.

Isoamylcyanamide, $C_8H_{17}NHCN$, was prepared, in good yield, by treating an ethyl acetate solution of isoamylamine (1 mol.) with a concentrated, aqueous solution of potassium cyanide (4 mol.) and to the whole, kept at from 5° – 10° , an ethyl acetate solution of bromine was slowly added with shaking. The ethyl acetate was separated from the water solution, washed with water, extracted with strong, 30 per cent sodium hydroxide, the resulting alkali solution cooled and made slightly acid with acetic acid, which caused an evolution of hydrocyanic acid, and the oil which separated was taken up with ether. The ether solution was washed several times with water, dried with calcium chloride and evaporated *in vacuo*, over concentrated sulphuric acid. A slightly colored oil remained which showed the properties of the monoalkylcyanamides. The oil was analyzed without further purification: Found, 24.46 per cent of nitrogen (Kjeldahl-Gunning); calculated for $C_8H_{17}N_2$, 25.03 per cent.

Attempts made to prepare cyanamides in a similar manner from amines, such as aniline, ethylaniline, etc., having the nitrogen atom attached directly to the benzene ring, were not successful. However, it was found that the method was readily applicable to the preparation of the corresponding cyanamides from benzylamine and piperidine.

Benzylcyanamide, $C_6H_5CH_2NHCN$, was prepared in the same way as isoamylamine except that the crystals, which separa-

¹ Ber. d. chem. Ges., 29, 2498 (1896).

ted from the alkali extract on adding acetic acid, were not taken up with ether, but instead were at once filtered off and dried on a clay plate.

The crystals gave a melamine on heating, or by standing at room temperature and had the solubilities given by Strakosch,¹ but, instead of melting at 33°, they melted at 43°. Strakosch crystallized the benzylcyanamide from ether and, as the cyanamide is *extremely* soluble in ether, it is probable that the low melting point of his product was due, in part, to traces of that solvent persistently held by the cyanamide. The yield was 90 per cent of the calculated.

Cyanpiperidine, $C_5H_{10}NCN$.—This was prepared in the same way as diethylcyanamide. The yield was 80 per cent, boiling at 102° (11 mm.). Analysis:

I. 0.1186 gram substance gave 26.45 cc. moist N at 17° and 746.4 mm.

II. 0.1092 gram substance gave 24.55 cc. moist N at 19°.5 and 749 mm.

	Calculated for $C_5H_{10}N_2$.	I.	Found. II.
N	25.49	25.51	25.52

Tests of the method, using acid amides, $RCONH_2$, instead of basic amines, RNH_2 and R_2NH , failed to give the acyl cyanamides, $RCONHCN$, desired.

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REPORT.

Tautomerism and Steric Hindrance.

At intervals during the past two years E. C. C. Baly, in conjunction with other chemists, has published a series of papers² containing the results of measurements of the ultra-violet absorption spectra of various organic compounds. From these observations they have deduced certain theoretical conclusions which are interesting and may prove to be of considerable importance in modifying the current views regarding tautomerism and steric hindrance. The spectra were deter-

¹ Ber. d. chem. Ges., 5, 694 (1872).

² J. Chem. Soc., 85, 1029 (1904); 87, 766, 1332, 1347, 1334 (1905); 89, 489, 502, 514, 618, 966, 982 (1906).

mined in the ordinary manner, except that the source of illumination was an arc light between iron poles. This arrangement had several advantages, the chief one being the large number of lines, which enabled the absorption bands to be measured with greater ease, and possibly with greater accuracy than had heretofore been the case.

The earlier experiments were carried out with acetylacetone, ethyl acetoacetate and certain of their derivatives, and it was found that neither the pure ketonic nor the pure enolic form of these compounds gives an absorption band but that a band is strongly developed when the two tautomeric forms of the ketone are present in equilibrium with one another. Thus, to take the case of ethyl acetoacetate, selective absorption is not due to the presence of either the form $\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$, or the form $\text{CH}_3\text{C}(\text{OH}) : \text{CHCO}_2\text{C}_2\text{H}_5$, but to both. Further, the absorption cannot be due to the wandering of the labile atom because the oscillation frequency of the light waves absorbed is practically the same whether this wandering atom be hydrogen, beryllium, sodium, or thorium. Moreover, it is impossible to draw any comparison between the oscillation frequencies of this labile atom and those of the light waves absorbed. These facts lead to the conclusion that the absorption of light is due to the *change of linking* indicated by the equation $\text{—CH}_2\text{CO—} \rightleftharpoons \text{—CH : C}(\text{OH})\text{—}$. The same idea may be expressed in another way by saying that in the passage from the ketonic to the enolic form and *vice versa*, the intermediate, transition phase —CHC— must have a momentary existence,



i. e., there must be an instant when the hydrogen, or other labile atom, is not linked to either carbon or oxygen and when both the carbon and oxygen linkages are undergoing rearrangement. The term *isorropesis* is applied to such oscillation. This theory appears to be in harmony not only with the results recorded in the papers under consideration, but also with those obtained by Hartley and others who have studied the connection between the absorption of light and change of linkage and also with Hewitt's theory of fluorescence.

A considerable number of other enol- keto- tautomerides, besides the two already mentioned, have been investigated by Baly and the work was then extended to the aromatic compounds. Hartley and Huntington¹ had observed 7 absorption bands in benzene, but Hartley and Dobbie² could only detect 6. Baly is able to confirm the presence of 7 bands, which he re-

¹ Phil. Trans., 170, i, 257 (1879).

² J. Chem. Soc., 73, 695 (1898).

gards as being due to the making and breaking of carbon linkages in benzene. If it be assumed that an even number only of carbon atoms are concerned in these changes, then not more than 7 transition phases are possible, *viz.*, 3 where two carbon atoms are concerned (*o*-, *m*- and *p*-), 3 when four carbon atoms are acting and 1 when all six of the carbon atoms change. This change in the linkages is supposed to be similar in all respects to that involved in the ketonic-enolic isomerism mentioned above.

The absorption of a considerable number of substitution products of benzene was determined and various regularities were observed, of which the following may be mentioned. The substitution of hydrogen by a single alkyl group produces an absorption which shows the first 2 benzene bands, the position of the remaining 5 being occupied by a single broad band. Other substituents produce greater changes. Of the derivatives of benzene with two saturated substituent groups, the para compounds are to be regarded as the most symmetrical, or, to put it in another way, the internal motions of the benzene molecule are less disturbed by para than by ortho or meta substitution.

In the third series of papers the subject of steric hindrance is taken up. This hypothesis was first brought into prominence by v. Meyer, who found that the esterification of diortho substituted benzoic acids, by means of alcohol and hydrogen chloride, became increasingly difficult as the mass of the substituent increased. The same has been found to be true of other reactions such as the hydrolysis of esters, nitriles, etc. On the other hand, Stewart¹ has shown recently that when a hydrogen atom near the carbonyl of a ketone is replaced by methyl there results a decrease in the additive capacity of the carbonyl group. This is what would be anticipated from the hypothesis of steric hindrance and yet there are difficulties against the acceptance of the latter idea. Thus, if a carbethoxy group, $-\text{CO}_2\text{C}_2\text{H}_5$, is substituted for hydrogen in the ketone, the additive power of the latter is increased and yet the mass of carbethoxy is nearly five times that of methyl. Experiments on the additive action of sodium hydrogen sulphite show that ketones which are semi-enolized react much more readily than those in which the carbonyl is intact. Further, the ortho disubstituted acids, which do not react with alcohol and hydrogen chloride, readily yield esters when their silver salts are treated with alkyl haloids, and yet it is not easy to regard the conditions of reaction as more drastic in the latter

¹ J. Chem. Soc., 87, 185 (1905).

than in the former case. As stated above, the *change* from the enolic to the ketonic form produces an absorption band in the ultra-violet, and this band is found to decrease proportionately to the diminution in the reactivity of the carbonyl group of the ketone.

An examination of a number of α -diketones, such as diacetyl, indicates that their yellow color is due to isorropesis between the carbonyl oxygen atoms in juxtaposition, the absorption being in the blue region of the spectrum. In general, the conclusion is reached that *it is quite untrustworthy to assume any fundamental difference in the constitution of compounds because one is colored and the other is white*. It is possible that color and fluorescence are both evidences of isorropesis; in the former case the isorropesis provides the mechanism and incident light actuates it; in the latter case isorropesis both provides and actuates the mechanism.

Similar results are obtained with the three nitroanilines and the three nitrophenols in neutral solution, and *p*-nitrophenol in alkaline solution. Under such conditions all these compounds have the quinonoid structure. Some interesting suggestions regarding the nature and configuration of the benzene ring are offered, but space is not available for their reproduction.

A later paper deals with the reactivity of substituted quinones. The results lead to the conclusion that the effect of substitution is to diminish potential tautomerism and thus, indirectly, isorropesis, while by unevenly loading the ring it produces, in benzoquinone, a greater tendency to assume the benzenoid form.

The last two papers hitherto published deal with isonitroso compounds and the phenylhydrazones of simple aldehydes and ketones, respectively, the results being of the same general character as those described above.

The idea of steric hindrance appears to be doomed; it has never been a very satisfactory hypothesis, partly from its rather crude mechanical nature and partly because there was a great temptation to use it to cover our ignorance of real causes and facts. Evidence against it of a purely chemical nature has been accumulating during the past few years, thus, for instance, the difficulty in obtaining the higher phenylated derivatives of methane, ethane, etc., has been shown to be simply a question of the method employed. A further point brought out in the papers under review is the fact that ketones apparently owe their reactivity to the presence of an enolic group, :C(OH)— or, at any rate, to what may be termed a "nascent," rather than a stable carbonyl group. The writer

of this report has been engaged for a considerable time on the investigation of camphoroxalic acid, by purely chemical methods. The results all point to the fact that the reactive group in this compound is the enolic :C(OH)— in the side chain, the true carbonyl of the original camphor nucleus being relatively very inert. It is interesting to have this view supported by conclusions obtained from experiments and properties entirely physical in their nature.

J. BISHOP TINGLE.

REVIEWS.

INTRODUCTION TO GENERAL INORGANIC CHEMISTRY. By ALEXANDER SMITH, Professor of Chemistry and Director of General and Physical Chemistry in the University of Chicago. New York: The Century Co. 1906. Price, \$2.25.

Text-books of inorganic chemistry for beginners usually contain 400 to 500 pages, and we may assume that this space is deemed sufficient, by the majority of teachers, for treatment of the matters absolutely essential to the beginner.

This book contains 780 pages, and a cursory examination will convince most teachers that it is too difficult for the average college student, taking the beginners' course, without previous training in science, although the author argues for such use. It should rather be ranked in the class of the larger text-books suitable for students who have some knowledge of the elements of chemistry and who have already done a little laboratory work.

A consideration of the modern text-books of this class shows that their authors employ the excess of space over the three or four hundred pages of essentials in widely differing ways. One discusses physical-chemical phenomena at great length. Another is mainly descriptive, and gives the latest methods of chemical manufacture and illustrated descriptions of improved apparatus in considerable detail. Other writers give much space to the study of constitution and to complex structural formulas. Finally, the use of the French text-books would lead the student to think that thermo-chemistry was the only chemical theory worthy of consideration. Now all of these books, without an exception, are very good in their way, are very interesting to chemists and repay fully the study bestowed on them by those who have some all-round knowledge of chemistry and chemical theory. We must not forget, however, that these books are not primarily written for our pleasure, but as the text-book for students, and that in most cases the text-book is the only book on chemistry which the average

college student seriously reads; hence he learns to regard chemistry from one aspect alone; nor is this corrected by the lectures, as the teacher generally chooses a text-book which mirrors his own way of teaching.

It is, therefore, with a feeling of great satisfaction that we find that Professor Smith's book cannot be classed in any one of the categories enumerated, but includes somewhat of them all. It is not a book to be lightly passed over. It is evident that the writer has given deep thought and great labor to the due apportionment of theory and fact, to the selection of theoretical matter, and to its introduction at the proper place. Quotations from the preface best explain Professor Smith's position.

"The principles of chemical equilibrium are (and have been for the past half-century) fully as much required for intelligent consideration of the simplest experiment, as is the theory of combining proportions itself. Important parts of the theories of solutions and of the battery are much more recent, but each is equally indispensable to the understanding of matters which cannot long be withheld from the notice of the beginner. Surely space ought not to be saved by entire omission of essential parts of the chief thing which makes chemistry at all worthy of a place among the sciences. Nor may we attain brevity, no matter how great the temptation, by condensing the passages on theory until they reach the limit of comprehensibility by an expert. Without clear exposition, full illustration and frequent application, laws and principles simply repel, or worse still mislead the beginner.

"The order of topics was determined by many considerations jointly. For example, in the first week of his work, a student may encounter experiments, in connection with which almost every part of chemical theory might usefully be discussed. But mastery of the theory must necessarily come bit by bit, and the theory is, therefore, distributed through the book. Instead of being introduced as soon as a fragment offers a chance for explanation, the treatment of each of the various theoretical subjects, as far as possible, has been postponed until a whole chapter could be devoted to it. The result makes subsequent reference easier and facilitates alterations in the order of study."

In the opinion of the reviewer, Professor Smith has succeeded in his task and has produced the best modern text-book on general chemistry for advanced students thus far published. University and college teachers should examine it.

By leaving but a narrow margin to the page, and using thin

but opaque and tough paper, the publishers have made the book not too thick and of convenient size. E. R.

EINFÜHRUNG IN DIE THERMODYNAMIK AUF ENERGETISCHER GRUNDLAGE. Von DR. JULIUS MEYER. Halle: Knapp. pp. 216. 1906. Price, M. 8.

In the preface of this most recent text-book on Thermodynamics the author states that he has designed it specially for students of chemistry and physical chemistry, and that his object in producing a new text-book, in a field where there already exist so many excellent works, is to offer one which is based on the reality of energy, and which is free, as far as possible, from matter which is not of special interest to the students concerned. The outline of the book is what one would expect, beginning with a discussion of energy, temperature and equations of state, and proceeding through the first and second principles of thermodynamics to various applications of formula to chemical reactions. The scope of the book is not unlike that of Buckingham's excellent treatise on Thermodynamics, and is not as wide as that of Planck's well-known work.

It must be confessed that the writer of the present review is thoroughly out of sympathy with the methods followed in this book. The discussion of energy, of temperature, of the properties of gases and of the second principle of thermodynamics seem to him to be hopelessly wrong. If one is willing to accept the various mathematical formulae and to regard the book as simply a discussion of the applications of these, it meets with the utmost approval. The illustrations taken from chemistry and physical chemistry are well chosen and are in every case the statements of our most recent knowledge. Therefore, as a book of reference for students who wish to obtain information concerning the agreement between theory and observation, it is to be recommended most highly.

J. S. AMES.

HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS, WITH SPECIAL REFERENCE TO PRACTICAL WORK. By J. W. MELLOR, D.Sc. Second edition enlarged. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 631. Price, \$4.50.

The appearance of the first edition of this valuable book has already been noticed.¹ The aim and object of the second edition is seen from the author's preface.

"In this edition, the subject-matter has been rewritten, and many parts have been extended in order to meet the growing tendency on the part of physical chemists to describe their ideas in the unequivocal language of mathematics."

¹ THIS JOURNAL, 29, 287 (1903).

The work was most timely, and the reviewer rejoices with the author in finding that there is such a large demand for it. The time has come when chemical facts, or at least a large number of them, can be expressed in mathematical language, and we have seen what magnificent progress has been the result.

This book undoubtedly makes mathematics accessible to a large number who have not the time, and often not the qualification for a more exact and extended study of the several branches of the subject. Further, Mellor has the happy faculty of selecting just those things which the students of the natural sciences ought to know. This is shown not only by the work now under consideration, but by his admirable book on "Chemical Statics and Dynamics."

Students of the natural sciences in general, and of chemistry in particular are urged to work through this splendid book.

H. C. J.

LA GRANDE INDUSTRIE CHIMIQUE. LE CHLORURE DE SODIUM, SEL MARIN, SEL GEMME, LES POTASSES ET LES SOUDES COMMERCIALES. Par H. PÉCHEUX, Professeur de physique et de Chimie à l'École Nationale d'Arts et Métiers d'Aix. Avec 26 Figures. Paris: Librairie J. B. Baillière et Fils. 1906. pp. 96. Price, 1.50 Fr.

This is one of twenty-four little books, the collection bearing the title "Encyclopédie Technologique et commerciale, collection nouvelle." If the other twenty-three volumes are like this it will form a unique work, for we have here a semi-popular monograph, written by a French government employee, professor in a national school, and our comment must be that it is incomprehensible that a reputable publisher should dare offer it to the public.

Just think of a monograph on the manufacture of sodium hydroxide, published in 1906, which makes no mention of electrolytic processes, and teaches the reader that the only commercial method is the action of slaked lime on sodium carbonate!

The only reference to the occurrence of salt in America is a line mentioning a deposit of salt in "the Rocky Mountains!" In the table of statistics, America is ignored, and astounding statements are made concerning production in Europe. In the following tables column A copies the figures given in this book of the average yearly production in metric tons. Column B gives the official figures, in short tons, for 1902, taken from the "Mineral Resources of the United States, 1904," published by the U. S. Geological Survey.

	A. Metric tons.	B. Tons.
United States	. . .	3,339,891
Great Britain	2,000,000	2,121,147
Russia	1,500,000	2,035,969
Austria	800,000	575,936
France	750,000	982,479
Germany	600,000	1,745,226

We see that, as a matter of fact, the United States leads the running enormously, Great Britain and Russia are neck and neck, with Germany rapidly gaining on them and France and Austria hopelessly out of the race. In this, as in several other industries, the relative rapid advance of the United States and Germany, as compared with other countries, is noticeable.

Further criticism of this book is unnecessary, but it is only fair to say that if it had been published in 1875 it would have been a respectable and fairly correct statement of the processes of the time, and the statistics would have been tolerably accurate for Europe at that date.

It should be further stated that it is probable that this volume is an unrevised reprint of an old book by a, possibly, dead author, so that M. Pécheux may be guiltless, but the publishers and compilers are inexcusable.

E. R.

FIRST SCIENCE BOOK. PHYSICS AND CHEMISTRY. By LOTHROP D. HIGGINS, PH.B., Instructor in Science in the State Normal School. Danbury, Conn. Boston: Ginn & Co. 1906. Price, 65 c.

A serviceable little manual for school use. One hundred and seventy pages are devoted to elementary physics and 58 to chemistry. There are many illustrated experiments, all very simple, which can be performed with little outlay for apparatus.

E. R.

LEHRBUCH DER GERICHTLICHEN CHEMIE. By DRS. GEORG BAUMERT, M. DENNSTEDT AND F. VOICHTLÄNDER. In two volumes. Braunschweig: Fr. Viewig und Sohn. 1906. Vol. II. pp. vii + 248 Price, M. 9.

The second volume of this work relates to the detection of forgeries in handwriting, to the examination of blood, etc. The part pertaining to forgeries in handwriting, in its chemical relations, refers particularly to the materials of ink. The inks which are used in old handwritings are described, and naturally the materials used for writings that represent old manuscripts should correspond to the inks in use at the time the manuscript must have been written. The microscopic tests are given in full and illustrated by photo-micrographs. In the chemical tests the behavior of the inks with water and their power of

copying with water and with hydrochloric acid, as also their behavior with other chemicals, is described. Special attention is given to their action with acid and alkaline reagents and with bleaching materials. Forgeries with lead pencil are also explained. Methods which are used for the mechanical and chemical removal of inks are described, and also for the mechanical removal of writing made by lead pencil. The methods that are used in determining whether all the writing on a page was made at the same time or at different ones are set forth in detail. An interesting chapter is devoted to means of deciding whether signatures are written by hand or produced by mechanical ways. The methods which should be used to decipher practically illegible writing are given. Processes for determining whether any secret marks—that is, those which are developed under certain conditions—have been used or not, are described.

Of special interest for legal purposes are the chapters devoted to the detection of blood and blood spots. The best methods of making photographs of blood spots are discussed in detail, as well as the peculiarities of blood and its differentiation from splotches of similar character. A very complete statement is made of all the standard methods now practiced for distinguishing between human blood and that of other animals. A chapter is also devoted to the action of poisonous gases on the blood. This volume will be found of particular interest to biological chemists and physiologists, who are called upon as expert witnesses before courts. H. W. W.

AMERICAN CHEMICAL JOURNAL

A CONTINUATION OF THE STUDY OF THE ACTION OF AMINES ON CAMPHOROXALIC ACID.

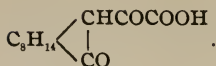
BY J. BISHOP TINGLE AND CHARLES J. ROBINSON.

INTRODUCTION.

In 1889, J. Bishop Tingle¹ discovered that camphor condenses with ethyl oxalate, in the presence of sodium, the product giving a deep violet-red color with ferric chloride, in alcoholic solution. This is in accord with the work of Claisen and his associates, showing that all ketones, RCOCH_3 and $\text{RCOCH}_2\text{R}'$, condense, in the presence of sodium, with esters, the latter type of ketone yielding the more stable products. All such condensation compounds obtained by Claisen give color reactions with alcoholic ferric chloride. Subsequent investigation² of the substance formed by the action of ethyl oxalate on camphor showed that it is the ester of an acid termed *camphoroxalic acid*, which was represented by the formula

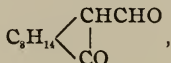
¹ Inaug. Diss., Munich, 1889, p. 34.

² J. Chem. Soc., **57**, 652 (1890).

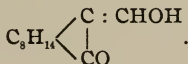


Later, when a general controversy arose as to whether 1,3-diketones are true diketones or unsaturated hydroxy derivatives, a more complete investigation of camphoroxalic acid was undertaken to determine, if possible, whether it has the "keto" or "enol" form, and to study the relative reactivity of the two ketone groups, or the enol and keto groups, the one in the side chain and the other in the ring.

The somewhat analogous compound formed by the action of ethyl formate on camphor, which was at first supposed to have a structure expressed by the formula



has been thoroughly investigated by Bishop, Claisen and Sinclair,¹ and shown to be



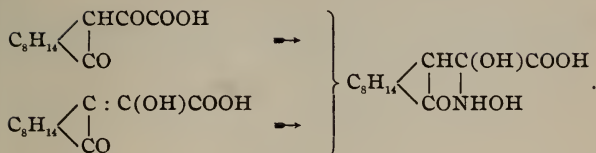
The name oxymethylene camphor was given to the substance by these authors. The work of Bishop Tingle and his associates on camphoroxalic acid² has brought to light facts indicating that it likewise has the unsaturated hydroxy structure, though the evidence cannot be considered conclusive. The chief facts hitherto discovered, which bear on the point, are :

1. The production of a stable addition product with hydroxylamine.³ The stability of the compound is such as to indicate that it is not simply an addition to a carbonyl group. It will be observed that addition to either the diketonic or ketoenolic form would give the same compound, as shown in the formula,

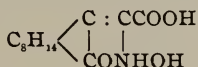
¹ ANN. CHEM. (Liebig), 281, 314.

² THIS JOURNAL, 19, 393 (1897); 20, 318 (1898); 21, 248 (1899); 23, 214 (1900). J. Am. Chem. Soc., 23, 363 (1901). THIS JOURNAL, 34, 217 (1905).

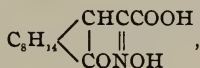
³ *Ibid.*, 19, 396, 408.



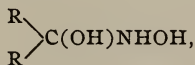
Such a substance might eliminate water in either of two ways, which would result in the formation of the compounds



and



respectively. This latter reaction, however, is simply an expression of the production of an oxime, and it is well known that oxime formation occurs very readily, without its being possible to isolate any intermediate, additive compound, *i. e.*, compounds of the formula

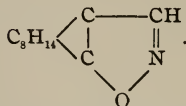


are, in general, highly unstable. The fact that Bishop Tingle's hydroxylamine additive compound was quite stable led him to the conclusion that it resulted from the addition of hydroxylamine to a double linkage in camphoroxalic acid, and, therefore, to regard this acid as being a ketoenolic compound and not a true diketone. This was the first example which had ever been observed of such an addition of hydroxylamine to a double linkage between two carbon atoms. Later, C. Harries¹ and his co-workers found that similar compounds could be obtained from mesityl oxide, phorone, etc.

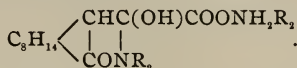
Attempts to dehydrate the camphoroxalic acid hydroxyl-

¹ Ber. d. chem. Ges., 30, 231 2726.

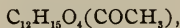
amine product led to the elimination of carbon dioxide and 2 molecules of water, and the formation of camphylisoxazole,¹



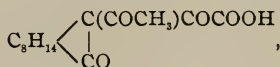
Camphoroxalic acid also forms addition products with diethylamine and dimethylamine² of the type,



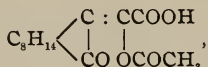
2. With acetic anhydride, a monacetyl derivative,



is produced.³ This might be either



or



but its formation by the direct action of acetic anhydride on camphoroxalic acid makes the latter structure appear more probable.

3. Camphoroxalic acid is hydrolyzed by barium hydroxide to camphor and oxalic acid,⁴ indicating the existence of a double linkage in the side chain.

4. Ethyl camphoroxalate and phenylhydrazine react⁵ to form what appears to be the hydrazone,

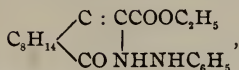
¹ THIS JOURNAL, 19, 409.

² *Ibid.*, 34, 246.

³ *Ibid.*, 20, 324.

⁴ *Ibid.*, 20, 327.

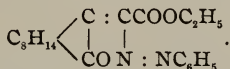
⁵ J. Chem. Soc., 57, 655. THIS JOURNAL, 19, 402.



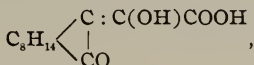
and not the hydrazone,



because, when it is oxidized by mercuric oxide or hydrogen peroxide, it yields a red, crystalline compound,¹



In view of these facts, the formula

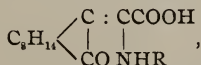


has been tentatively assigned to camphoroxalic acid. The work of Baly and his collaborateurs on the optical properties of enolic and ketonic compounds, of which a review and bibliography has been given recently,² lends a considerable amount of support to the conclusion reached, from purely chemical considerations, by the senior author of this paper, that the point of attack in such compounds is the group C : COH and not CO.

The simple reaction products with primary amines are believed to have the general structure,



when addition products are formed, and

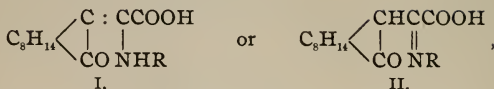


when a molecule of water is eliminated in the reaction.

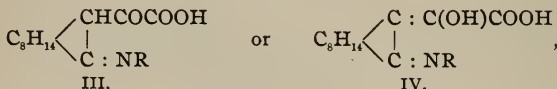
¹ THIS JOURNAL, 20, 338; 21, 258.

² *Ibid.*, 36, 213.

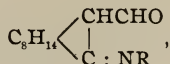
The hypothesis that compounds



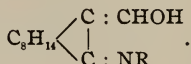
and not



are produced, is supported by the fact that, when heated, the substances in question give up carbon dioxide, forming neutral products. Compounds of the latter type, where carboxyl is joined to —CO— or >C(OH)— , would not be expected to eliminate carbon dioxide; and, if they did, the products would be aldehydes,



or oxymethylene compounds,



The inactivity and neutrality of the substances actually obtained discredit the possibility of such a structure and leave the choice between the first two formulas. For the reasons discussed above, the former of these, I., is preferred.

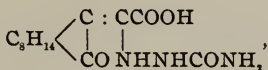
A somewhat extensive investigation of the action of amines, of various types, on camphoroxalic acid has already been made.¹ The present paper contains the results of a continuation of this study. The amines which have been employed are semicarbazine, urea and the methylated ureas, hydrazine, phenylhydrazine and parabromophenylhydrazine. In the course of this investigation, additional evidence indicative of the unsaturated hydroxy structure has been found.

¹ *Vide* Table, THIS JOURNAL, 34, 236.

THEORETICAL.

The Action of Semicarbazine on Camphoroxalic Acid.

In a preliminary experiment on the action of semicarbazine on camphoroxalic acid, J. Bishop Tingle and Alfred Tingle¹ obtained what appeared to be two isomeric derivatives of the formula



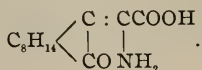
one of which was found to melt at 218° and the other at 209°–210°. The two were separated by the solubility of the former in ether. Subsequently, Bishop Tingle and W. E. Hoffman, Jr.,² obtained, under different conditions, a compound of the same formula which, when crystallized from alcohol, melted at 200°, but when crystallized from glacial acetic acid, melted at 209°–210°. Nothing further was done with these substances at that time. To clear up the apparent discrepancy, we have repeated the two earlier experiments and have compared the products carefully, with the result that the supposedly isomeric substances are proved to be identical. The variation in the melting points recorded in the previous work was found to be due to the exhibition, by the compound, of a remarkable sensitiveness not only to the rate of heating, but also, apparently, to small amounts of impurities. Experiments showing the degree of variation due to differences in the rapidity of the heating are tabulated on page 256, the observed melting point varying from 200°.5, when the rate of heating above 190° was 2° per minute, to 217° when the rate was 15° per minute. The presence of a small amount of resinous matter, not sufficiently large to be detected by analyses, was found to render the substance somewhat soluble in ether, which explains the separation into two portions that was effected by Bishop Tingle and A. Tingle.

The compound was designated in the latter of the two papers mentioned above as "semicarbazine camphoformencaminecar-

¹ THIS JOURNAL, 23, 224 (1900).

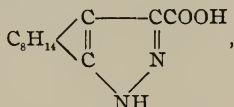
² *Ibid.*, 34, 251 (1905).

boxylic acid." The name *carbamylcamphoformeneaminecarboxylic acid* seems preferable, as showing more clearly the relation to the simpler compound, *camphoformeneaminecarboxylic acid*,

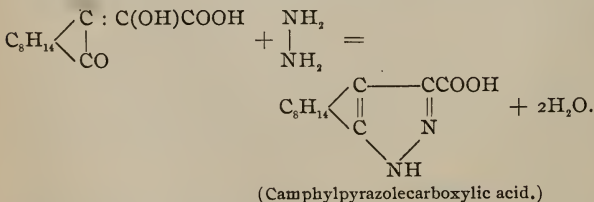


The term "carbamyl" designates satisfactorily the carbamide residue, —NHCONH_2 , which is present.

When camphoroxalic acid and semicarbazine react at 125° , under pressure, the products are hydrazodicarbonamide, $\text{H}_2\text{NCONHNHCONH}_2$, and *camphylpyrazolecarboxylic acid*,

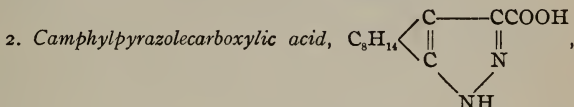


both of which are also products of the fusion of carbamylcamphoformeneaminecarboxylic acid (see below). The formation of these compounds, under the conditions employed, is explained by the fact that semicarbazine breaks down under the influence of heat into hydrazodicarbonamide and hydrazine. The hydrazine then interacts with camphoroxalic acid. The reactions may be expressed thus :



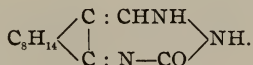
At least three compounds are formed by the fusion of carbamylcamphoformeneaminecarboxylic acid, *viz.* :

1. Hydrazodicarbamide, $\text{NH}_2\text{CONHNHCONH}_2$, which is insoluble in all the ordinary, neutral, organic solvents, and but slightly soluble in boiling water. It melts at 245° and has been previously obtained from semicarbazine by the elimination of hydrazine.¹ The insoluble compound, melting at 255° , which is mentioned by Bishop Tingle and A. Tingle² as being obtained in small amount, was, no doubt, this same substance. It melts at 245° only when heated very slowly.



which melts at 255° – 258° . The fact that the same compound is obtained by the action of hydrazine on camphoroxalic acid confirms the view that it has the above structure.

3. A compound crystallizing from alcohol in yellow needles, which melt at 305° – 306° . It has the composition of carbamylcamphoformeneaminecarboxylic acid minus the elements of water and carbon dioxide, and is, without doubt, represented by the formula



It may be called *camphyl-3-keto-1,2,4-heptatriazine*.

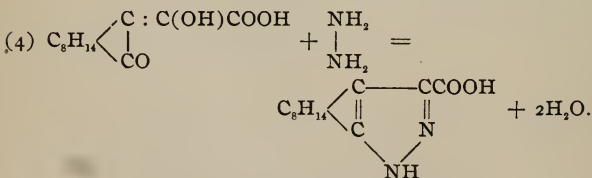
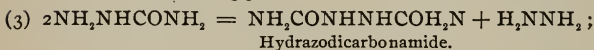
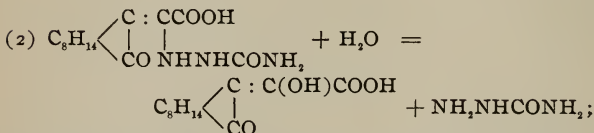
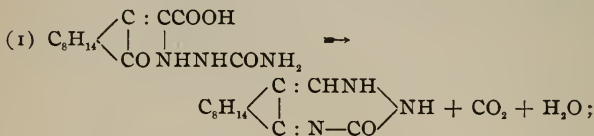
The action of heat on carbamylcamphoformeneaminecarboxylic acid is best explained, we believe, by the following hypothesis: A portion of the compound eliminates water and carbon dioxide and forms the substance melting at 305° – 306° . The water thus formed hydrolyzes another portion of the original substance into its components, semicarbazine and camphoroxalic acid. The reaction then proceeds in the same way as when these two substances are heated together under pressure, hydrazine being formed and condensing with camphoroxalic acid. This condensation involves the elimination of water, which hydrolyzes some of the original compound, and

¹ Thiele: Ann. Chem. (Liebig), **270**, 45. Curtius: Ber. d. chem. Ges., **27**, 57.

² THIS JOURNAL, **23**, 228.

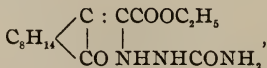
the greater the extent of the hydrolysis the larger the amount of water subsequently formed. With water present, hydrolysis would be expected to take place more readily than condensation to the 7-membered ring compound, camphylketoheptatriazine. This explains the fact that the latter substance was obtained in very small amount.

The following equations express the reactions involved :



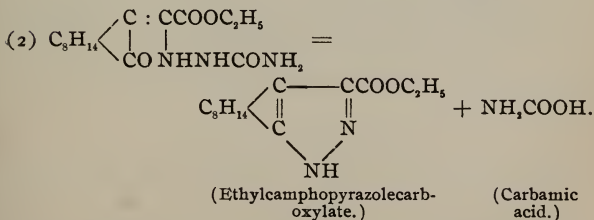
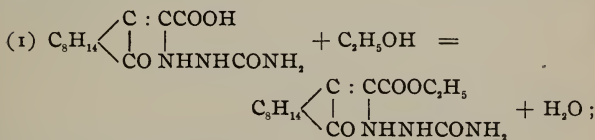
Camphylpyrazolecarboxylic acid.

Experiments were also made on the action of dry hydrogen chloride on carbamylcamphoformeneaminecarboxylic acid, in the presence of absolute alcohol. If the reaction is carried out at about 0° , the primary product is *ethyl carbamylcamphoformeneaminecarboxylate*,



which melts at 191° . The same compound has been described

by Bishop Tingle and A. Tingle,¹ who prepared it by the action of semicarbazine on ethyl camphoroxalate. Their preparation melted at 202°. This difference in melting point is doubtless due to differences in the rapidity of heating, a behavior which is so markedly shown in the case of the acid. When this ester is allowed to stand in the alcoholic hydrochloric acid solution in which it was made it soon decomposes, and ethyl camphylpyrazolecarboxylate is formed, which melts at 91°-92° and crystallizes from ligroin in magnificent, monoclinic, tabular crystals. This ester is strongly basic and forms a stable hydrochloride, that softens at 151° and melts at 156°. Camphylpyrazolecarboxylic acid itself is basic to the extent of dissolving in dilute, aqueous acids, though nearly insoluble in water. The action of hydrochloric acid and alcohol on carbamylcamphoformeneaminecarboxylic acid is represented in the following equations:



As carbamic acid, in the presence of hydrochloric acid, would cause the formation of ammonium chloride, which was not observed, it is probable that urethane, $\text{NH}_2\text{COOC}_2\text{H}_5$, was the actual product of the reaction, though its presence was not proved, because our interest was confined chiefly to the other substances involved. The shifting of the double bonds ob-

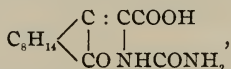
¹ THIS JOURNAL, 23, 227.

served in the above formula, representing the formation of a pyrazole derivative, requires no comment, as it is well known that such rearrangement occurs generally in pyrazole formation.¹

The Action of Urea and of the Methylated Ureas on Camphoroxalic Acid.

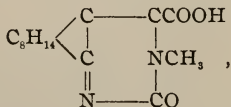
J. Bishop Tingle and W. E. Hoffman, Jr.,² found that when urea and camphoroxalic acid are heated together no compound could be isolated from the tarry reaction product. Under different conditions, we have succeeded in obtaining a urea derivative and also derivatives of methylurea and the symmetrical dimethylurea.

When camphoroxalic acid and urea, in alcoholic solution, are heated under pressure, at 135°, a simple condensation takes place and *formamidylcamphoformeneaminecarboxylic acid*,



is formed. It melts at 192°–194°.

When camphoroxalic acid and methylurea are heated together, without a solvent, or when an alcoholic solution of these substances is heated under pressure, at 100°, condensation takes place with elimination of 2 molecules of water, the product being *1-methyl-2-keto-4,5-camphylmetadiazine-6-carboxylic acid*,



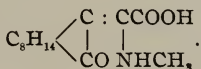
which melts at 154° and is deposited from ethyl acetate solution in slightly yellow, long, prismatic crystals. The fact that a secondary amine group condenses with camphoroxalic acid is significant, and could scarcely be explained on any other basis than that of the unsaturated hydroxy structure of the

¹ Knorr: Ann. Chem. (Liebig), 279, 188.

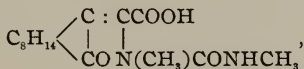
² Loc. cit.

latter. It is also noteworthy that the condensation takes place much more readily than with urea itself. This is, perhaps, to be attributed to the more basic character of an alkylated amine as compared with the simpler compound. The influence of methyl in one of the amine groups evidently extends also to the second amine, for we find it entering into reaction, whereas, in the case of urea, the second amine group is unaffected under similar conditions.

Symmetrical dimethylurea and camphoroxalic acid react readily when a methyl alcoholic solution of the two substances is heated, under pressure, at 100° . There is difficulty in isolating the substance which is formed on account of the tarry nature of the mixture of reaction products; finally, however, a small quantity of a compound was obtained which melted at 104° – 105° . A larger amount of a second compound, melting at 77° – 78° , was also isolated; it proved to be *methylcamphorformeneaminecarboxylic acid*,



This may have been produced either by the action of methylamine resulting from the decomposition of a part of the dimethylurea during the heating, or, on the other hand, a dimethylurea derivative of camphoroxalic acid, such as



may have been first formed, and then hydrolyzed to the methylamine compound by the treatment employed in the attempts to isolate the product. The fact that the odor of methylamine was not at first perceptible, but developed during this process, and the further fact that a small amount of an unknown compound actually separated, makes the second hypothesis appear the more probable. Hydrolysis of the methylurea compound formulated above would, presumably, yield carbon dioxide, methylamine and methylcamphorformeneaminecarboxylic acid. The latter substance, which, as already mentioned, was

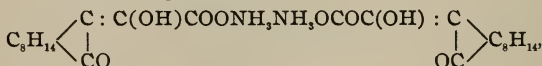
actually obtained, is the missing member of the series of methylamine derivatives of camphoroxalic acid which Bishop Tingle and W. E. Hoffman, Jr.,¹ were unable to prepare under the conditions employed by them.

All attempts to get condensation products of camphoroxalic acid and the unsymmetrical dimethylurea were unsuccessful.

The Action of Hydrazine on Camphoroxalic Acid.

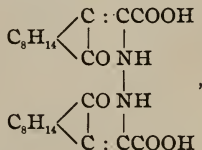
Bishop Tingle and W. E. Hoffman, Jr.,² failed to obtain any reaction when camphoroxalic acid, hydrazine hydrochloride and sodium hydroxide were dissolved in alcohol and heated on the water-bath. The use of barium hydroxide in place of sodium hydroxide gave a similar result. We find that a methyl alcoholic solution of free hydrazine, prepared essentially as described by Lobry de Bruyn,² reacts, at the ordinary temperature, with camphoroxalic acid, yielding three products :

1. *Hydrazine camphoroxalate,*



when in a dry condition, this is a stable salt. It begins to decompose only at 186°, but in solution it dissociates when gently warmed, and the liberated hydrazine condenses with 2 molecules of the acid. Aqueous sodium carbonate also decomposes it, and acidification yields the condensation product, bīcamphoformeneaminecarboxylic acid.

2. *Bīcamphoformeneaminecarboxylic acid,*



is obtained by the condensation of 1 molecule of hydrazine with 2 molecules of camphoroxalic acid. It is a yellow sub-

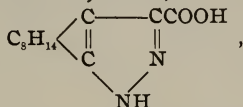
¹ THIS JOURNAL, 34, 249.

² Rec. Trav. Chim., 13, 433.

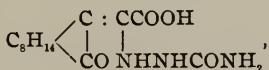
stance which decomposes, without complete fusion, at 150° – 155° .

When crystallized from methyl alcohol, it takes up 2 molecules of the alcohol, which are not readily expelled. The crystallized product has a different appearance and different solubilities from the dried substance, and it begins to decompose at 137° . It appears, therefore, that the 2 molecules of solvent are held in closer combination than is usually the case with solvent of crystallization. This is a strong indication of unsaturation in the molecule.

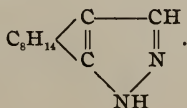
3. *Camphylpyrazolecarboxylic acid*,



is formed by the condensation of 1 molecule of hydrazine with 1 of camphoroxalic acid. It melts at 255° – 258° . The same compound was obtained, as previously mentioned, from carbamylcamphoformeneaminecarboxylic acid,

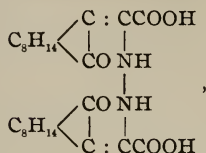


when it is decomposed by heat; its ester was formed by the action of dry hydrochloric acid gas on the same compound, in absolute alcoholic solution. From the facts detailed below, there can be little doubt that this substance is a pyrazole derivative as represented in the above formula. When fused, carbon dioxide is eliminated, and the resulting compound gives a violet color if reduced with alcohol and sodium, and subsequently oxidized with nitric acid and potassium bichromate, indicating that it is *camphylpyrazole*,



This substance remains unmelted up to temperatures as high as 288° .

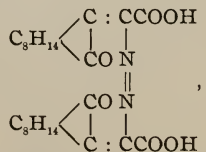
The behavior of biscamphoformeneaminecarboxylic acid,



at high temperatures was then investigated. It was found that at least 3 substances are formed, but a complete study of them has not, as yet, been made. The details of the separation of these compounds from the fused material are given in the experimental part, p. 273; eventually the following products were isolated:

1. A *compound*, $\text{C}_{24}\text{H}_{30}\text{O}_6\text{N}_2$, which differs from the parent material, $\text{C}_{24}\text{H}_{32}\text{O}_6\text{N}_2$, by containing 2 atoms of hydrogen less. This substance crystallizes from ethyl acetate in nodular clusters of fine needles, which have a light yellow color and melt at 222° – 223° . The body is an acid, but nothing further was learned regarding its constitution.

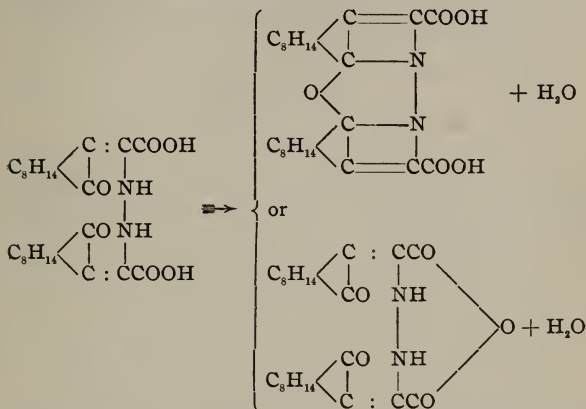
2. A *compound*, which is also an acid and is isomeric with the preceding substance. It melts at 232° and has a dull yellow color, but is usually tinged with red, and its solutions, on standing, become red and deposit red crystals which have practically the same melting point as the yellow substance. The colored material may, perhaps, have an azo structure, such as



but as the pure compound is only slightly colored, this particular formula would hardly apply to it.

3. A *compound*, the analysis of which gave the formula

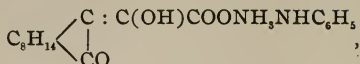
$C_{24}H_{30}O_5N_2$. The substance was, however, obtained in such small quantity that the results require confirmation. If this formula should prove to be correct, the substance is formed from the parent compound, biscamphoformeneaminicarboxylic acid, by elimination of water, thus:



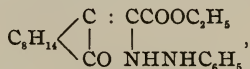
So far as our limited knowledge permits the expression of an opinion, we incline to favor the first of these formulas. The substance crystallizes from ethyl acetate in light yellow, translucent prisms, which melt at 221° . The quantity of material available was too small to permit a more thorough examination of this compound at present, but in the immediate future it is planned to continue the investigation of all three of these substances in this laboratory.

The Action of Phenylhydrazine on Camphoroxalic Acid.

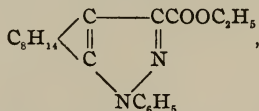
In view of the results which were obtained by the action of hydrazine on camphoroxalic acid, it appeared desirable to extend the investigation to the action of phenylhydrazine on camphoroxalic acid. In the course of some work on the subject, Bishop Tingle had prepared the following derivatives of this base:

1. Phenylhydrazine camphoroxalate (?),¹

melting at 214°–215°, with previous darkening. This had been prepared only once, in very small quantity, and had not been analyzed.

2. Ethyl camphoroxalate phenylhydrazide,²

prepared by condensing ethyl camphoroxalate and phenylhydrazine. It melts at 212°. The corresponding methyl ester was also obtained from methyl camphoroxalate.³

3. Ethyl camphylphenylpyrazolecarboxylate,⁴ m. p. 114°,

and the corresponding methyl ester,⁵ m. p. 80°.5–81°.5, were prepared by the condensation of the respective phenylhydrazides with dehydrating agents.

4. Camphylphenylpyrazolecarboxylic acid,⁶ m. p. 197°, was derived by hydrolysis from both of the preceding esters.

In the course of the present investigation we have obtained camphylphenylpyrazolecarboxylic acid directly from camphoroxalic acid. In addition, it has been found possible to isolate a new compound, the primary reaction product when camphoroxalic acid, or potassium camphoroxalate and phenylhydrazine are brought together at the ordinary temperature. This is the *addition compound*,

¹ THIS JOURNAL, 20, 328 (1898).

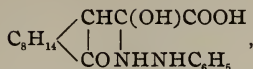
² J. Chem. Soc., 57, 655 (1890). THIS JOURNAL, 19, 402 (1897); 20, 338 (1898); 21, 258 (1899).

³ *Ibid.*, 20, 335.

⁴ *Ibid.*, 19, 403.

⁵ *Ibid.*, 20, 336.

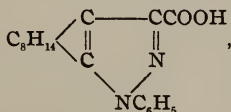
⁶ *Ibid.*, 19, 405; 20, 336.



which melts at 120° and crystallizes in very fine, yellow needles. It is quite stable, and can be boiled in weakly dissociating solvents like ether, chloroform and benzene without decomposition. Over sulphuric acid, in a vacuum desiccator, it remained unchanged after standing for 2 months. The possibility of the compound being a salt is excluded by its formation from potassium camphoroxalate.

The stability of this addition compound is another strong argument in favor of the unsaturated hydroxy structure for camphoroxalic acid. A few addition products of phenylhydrazine with true ketones have been isolated; several esters of oxalacetic acid¹ and of dioxysuccinic acid² form such derivatives when the reaction takes place at a low temperature, but otherwise, by the elimination of water, the reaction proceeds to the formation of phenylhydrazones. The addition compounds of the esters of dioxysuccinic acid lose water when left standing either alone, or covered with ether or alcohol. The corresponding compound with ethyl oxalacetate is changed to the hydrazone by warming its solutions; and when it was allowed to remain for 12 days, in a vacuum desiccator, over sulphuric acid, it was quantitatively transformed to the phenylhydrazone. It is evident, therefore, that the addition compound with camphoroxalic acid is not to be classed with the addition products of true ketones and phenylhydrazine.

This compound, after being boiled for some time with alcohol, or when fused, condenses to camphylphenylpyrazolecarboxylic acid,



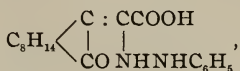
the melting point of which was observed to be 196° instead of

¹ W. Wislicenus and Max Scheidt: *Ber. d. chem. Ges.*, **24**, 3006 (1891).

² Anschütz and Pauly: *Ibid.*, **28**, 66 (1895).

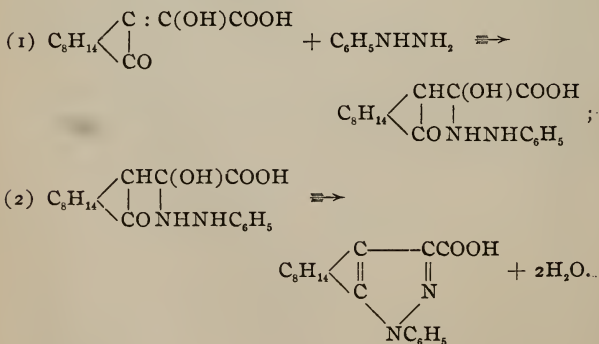
197°, as previously recorded. In the former description of this substance,¹ it was noted that crystals containing 0.5 molecule of benzene were deposited from that solvent. It is now found that the compound crystallizes very readily from alcohol with 1 molecule of alcohol of crystallization.

Attempts to eliminate 1 molecule of water from the addition compound, so as to form the phenylhydrazide of camphoroxalic acid,



were unavailing. The condensation always went further, and 2 molecules of water were eliminated, giving the pyrazole derivative. Unsuccessful attempts were also made to obtain the "phenylhydrazine camphoroxalate" previously described. It appears, therefore, that the formation of this substance, whatever be its nature, depends on some slight variations of experimental conditions which were not noted at the time when the original experiment was carried out, and which we have been unable to reproduce.

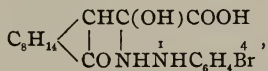
The action of phenylhydrazine on camphoroxalic acid may be expressed by the equations:



¹ *Loc. cit.*

The Action of Parabromphenylhydrazine on Camphoroxalic Acid.

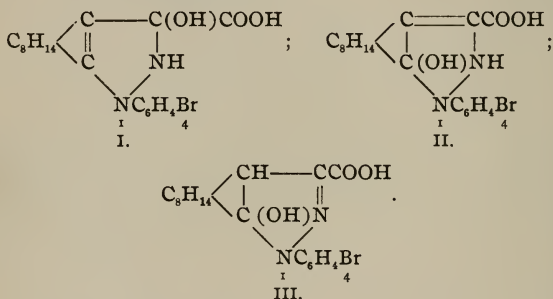
We extended the investigation so as to include a study of the action of parabromphenylhydrazine on camphoroxalic acid, partly in order to ascertain the effect of the negative bromine atom on the properties and stability of the condensation products, and partly in the hope of preparing some substances belonging to types which were not represented by the compounds which we had succeeded in isolating from hydrazine and from phenylhydrazine. As the result of our experiments, the following 5 derivatives have been obtained :

1. *An addition compound,*

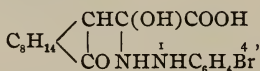
corresponding to the addition compound obtained with phenylhydrazine. It is formed, together with the next compound described, whenever parabromphenylhydrazine and camphoroxalic acid are brought together in solution, at the ordinary temperature, and the reaction proceeds in the same way when the solution is heated. The substance melts at 149° and crystallizes in fine, yellow needles—a deeper yellow than that of the corresponding phenylhydrazine derivative. The stability of the compound is such that it is unaffected by heating with acetic anhydride, on the water-bath, for an hour. No products formed by the addition of amines to aldehyde or ketone groups have shown a comparable degree of stability, and although the facts can best be explained by supposing that the addition has taken place at the double linkage in the group $>\text{C}:\text{COH}-$ (*vide* pp. 225, 227), yet it does not account for this stability.

2. The second compound, which is always obtained with the preceding one, melts at 172° . In some experiments, compound number 1 separated first from the solvent, and then the second substance; in other experiments the order of separation was exactly reversed, and sometimes both compounds came down simultaneously. We were unable to ascertain exactly what conditions determine which substance shall precipitate first. This behavior furnishes another illustration of the considera-

ble differences in results which are brought about by relatively minute variation in the experimental conditions, a fact that must be constantly kept in mind in dealing with substances belonging to this class. The compound under discussion differs in composition from the additive compound by 1 molecule of water; but in the fact that it is not vigorously attacked by concentrated nitric acid, and in its crystallizing power, it resembles the pyrazole derivatives rather than the hydrazides. It appears, therefore, to have the constitution expressed by one of the following formulas:

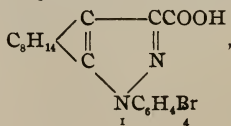


The addition compound being



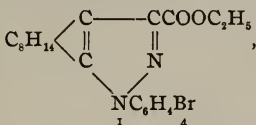
it seems most probable to suppose that the second nitrogen atom combines with the carbonyl of the camphor ring, with the elimination of water, which would then give the structure represented in Formula I. Further work will be necessary to decide this point.

3. *Camphylparabromphenylpyrazolecarboxylic acid,*

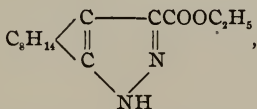


melting at 215° , is formed when either of the two compounds just described is fused. It is interesting to note that the addition compound loses 2 molecules of water at once, instead of first losing 1 molecule and forming the intermediate product, (2) although the latter is a very stable substance. The same conduct is characteristic of the addition compound with phenylhydrazine. This compound (m. p. 215°) is colorless, and crystallizes from benzene in nodular clusters of minute needles.

4. *Ethyl camphylparabromphenylpyrazolecarboxylate*,

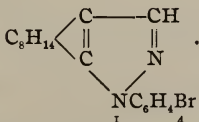


was obtained by treating the addition compound, m. p. 149° , with absolute alcohol, saturated with dry hydrochloric acid, at 0° . It melts at 107° and crystallizes from acetone in magnificent, triclinic crystals. In contrast to ethyl camphylpyrazolecarboxylate,



this substance shows no basic properties.¹

5. A compound, not analyzed, which is probably *camphylparabromphenylpyrazole*,



It is formed by fusing camphylparabromphenylpyrazolecarboxylic acid, carbon dioxide being eliminated. The substance is extremely soluble in all the ordinary organic menstua, and remains as a gummy mass after the solvent has evaporated

¹ Vide p. 233.

spontaneously. It was not found possible to purify the body sufficiently for analysis.

Of these five compounds, it is seen that the first two have an important bearing on the structure of camphoroxalic acid and tend to confirm the unsaturated hydroxy formula.

The Hydration Product of Camphoroxalic Acid.

In order to obtain, if possible, further evidence of the unsaturated character of camphoroxalic acid, an investigation was undertaken of the hydration product obtained by Bishop Tingle¹ when the acid is heated, under pressure, with aqueous solutions of mineral acids. The substance in question has the composition of camphoroxalic acid plus 2 molecules of water and, in alcoholic solution, gives a blue color with ferric chloride. It was prepared by the use of sulphuric acid as described in the earlier paper², but difficulty was experienced in working with it because of its extremely ready reversion to camphoroxalic acid. It was found that 4 equivalents of sodium carbonate are required to neutralize it, which indicates that there are 3 hydroxyls present, besides the carboxyl. This confirms the analysis previously published³ and indicates that the water is not present as water of crystallization.

With aniline and semicarbazine, respectively, at the ordinary temperature, products were formed which were found to be identical with the corresponding camphoroxalic acid derivatives, but with hydroxylamine, what appears to be a new substance was obtained which melts at 181°-182°, but has not been investigated. The work was not pushed further because of the difficulty of obtaining the pure hydrated acid in quantity.

Summary of the Points Bearing on the Structure of Camphoroxalic Acid.

In the introduction to this paper, several facts were mentioned⁴ as having contributed to the belief that camphoroxalic

¹ THIS JOURNAL, 20, 329 (1898).

² *Loc. cit.*

³ *Loc. cit.*

⁴ *Vide p. 224.*

acid is not a true diketone, but an unsaturated hydroxy ketone, *viz.* :

1. The production of a stable addition product with hydroxylamine; and also the formation of addition products with diethylamine and dimethylamine.
2. The formation of a monacetyl derivative with acetic anhydride.
3. The hydrolysis with barium hydroxide, yielding oxalic acid and camphor.
4. The production of a phenylhydrazide instead of a phenylhydrazone.

In this investigation the following additional facts have been discovered which tend to confirm the unsaturated hydroxy structure:

1. Methylurea reacts readily with camphoroxalic acid—much more readily than does urea itself. Both the primary and secondary amine groups enter into the condensation, forming a metadiazine derivative. The condensation of a secondary amine group with a ketone is less easily explained than its reaction with the group $>\text{C}:\text{C}(\text{OH})-$. Symmetrical dimethylurea also appears to react with camphoroxalic acid, and Mr. Williams, in this laboratory, has prepared a condensation product with symmetrical acetylphenylhydrazine, both of which facts argue for the enolic form of the acid.

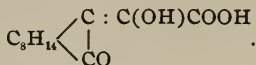
2. Camphoroxalic acid yields an addition product with phenylhydrazine, which is much more stable than any addition products from true ketones which have ever been observed hitherto.

3. Parabromphenylhydrazine yields a still more stable addition product.

4. With parabromphenylhydrazine a ring compound is obtained in which both the keto (or the keto and the enolic) groups have reacted, but with the elimination of only 1 molecule of water. These last three facts are entirely beyond the range of common experience with ketones, and must be explained by the enolic hypothesis.

The general result of this investigation has been, therefore,

to strengthen the view that camphoroxalic acid should be represented by the formula

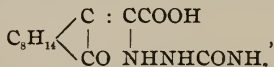


The various derivatives thus far obtained by the action of the amines studied in this investigation are represented in the following table, pp. 249-253, and the relations existing between them are indicated.

EXPERIMENTAL.

In the preparation of camphoroxalic acid, one or two minor changes were made in the method as described by Bishop Tingle and W. E. Hoffman, Jr.¹ Instead of 400 cc. of petroleum ether for each portion of the reacting substances, 350 cc. were used, and satisfactory results were obtained. In distilling the petroleum ether from the reaction product, sufficiently diminished pressure was employed to keep the temperature of the liquid in the flask below 110° to the end of the operation. No difficulty was experienced in accomplishing this with the ordinary water suction-pump. Otherwise the substance was prepared exactly as described by the authors mentioned.

The Supposedly Isomeric Semicarbazine Derivatives of Camphoroxalic Acid.—In the course of some earlier work on camphoroxalic acid derivatives, J. Bishop Tingle and Alfred Tingle² found what appeared to be two isomeric compounds,



formed when semicarbazine hydrochloride (2 mols.), camphoroxalic acid (1 mol.) and potassium hydroxide (3 mol.) were heated at 100°, for 4 hours, in a closed tube, with alcohol as a solvent. One substance was described as soluble in ether, and melted at 218° when crystallized from acetone; the other was insoluble in all neutral, organic media, and melted at 209°-210° when crystallized from glacial acetic acid. In a later

¹ THIS JOURNAL, 34, 235 (1905).

² *Ibid.*, 23, 224 (1900).

Table I.—Derivatives of Camphoroxalic Acid with :

SEMICARBAZINE.

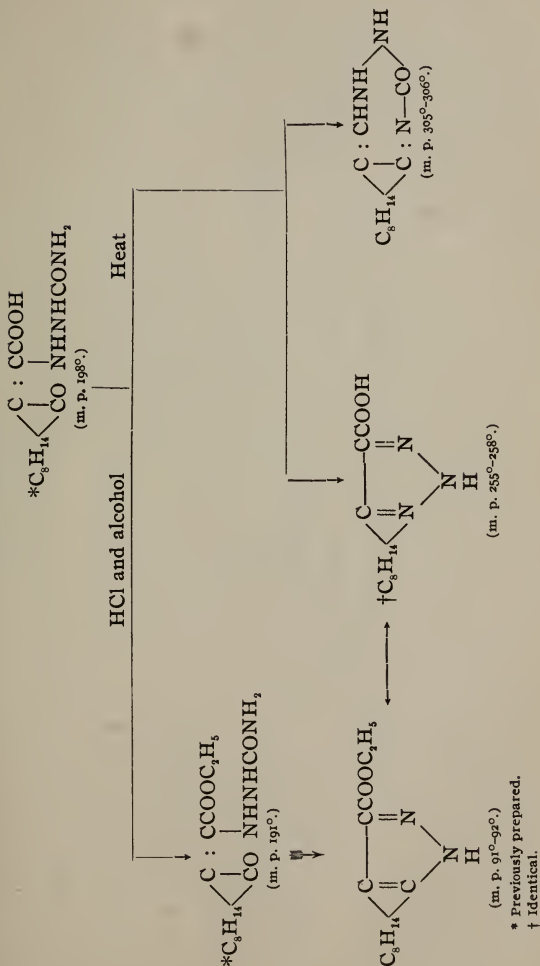
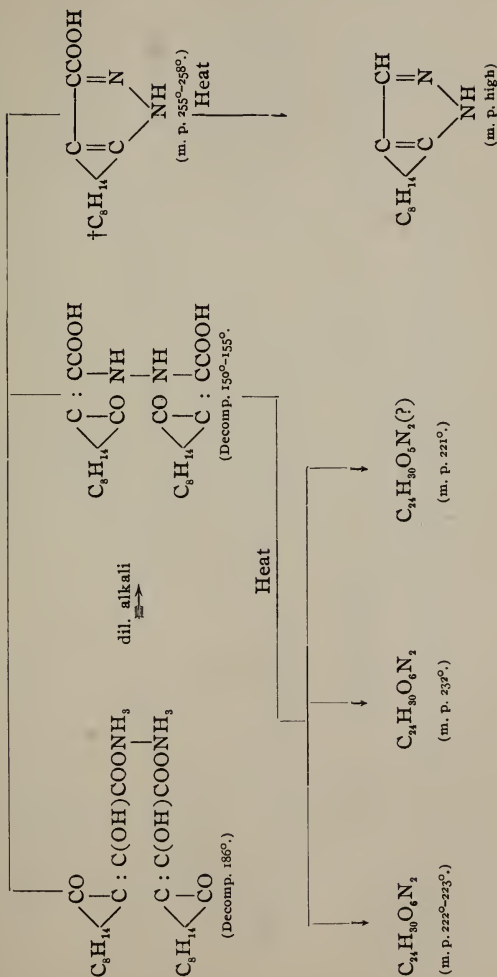


Table I.—Derivatives of Camphoroxalic Acid with (Continued):

UREA.	METHYLUREA.	SYM. DIMETHYLUREA.	UNSYM. DI-METHYLUREA.
$\begin{array}{c} \text{C}_8\text{H}_{14} \diagdown \\ \text{C} : \text{CCOOH} \\ \\ \text{CO} \text{ NHCONH}_2 \\ \text{(m. p. } 192^\circ\text{--}194^\circ\text{.)} \end{array}$	$\begin{array}{c} \text{C}_8\text{H}_{14} \diagdown \\ \text{C} = \text{CCOOH} \\ \quad \\ \text{C} \quad \text{NCH}_3 \\ \quad \\ \text{N} \quad \text{CO} \\ \text{(m. p. } 154^\circ\text{.)} \end{array}$	$\begin{array}{c} \text{C}_8\text{H}_{14} \diagdown \\ \text{C} : \text{CCOOH} \\ \quad \\ \text{CO} \quad \text{N(CH}_3\text{)CONHCH}_3 \\ \text{(m. p. } 104^\circ\text{--}105^\circ\text{.)} \end{array}$	—
		$\begin{array}{c} \text{C}_8\text{H}_{14} \diagdown \\ \text{C} : \text{CCOOH} \\ \quad \\ \text{CO} \quad \text{NHCH}_3 \\ \text{(m. p. } 77^\circ\text{--}78^\circ\text{.)} \end{array}$	

Table I.—Derivatives of Camphoroxalic Acid with (Continued):

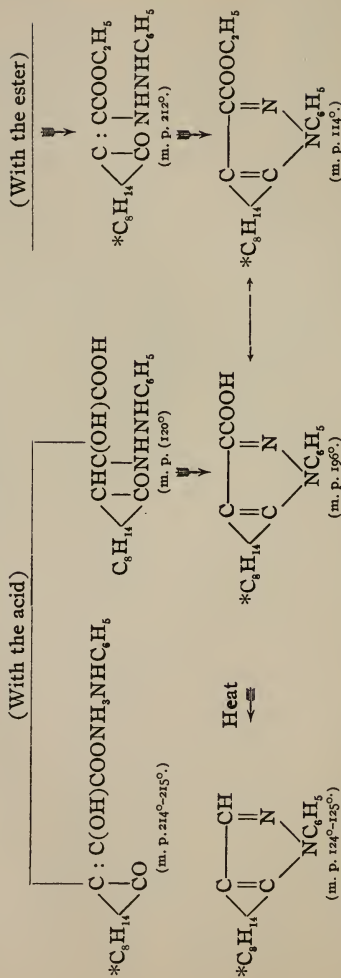
HYDRAZINE.



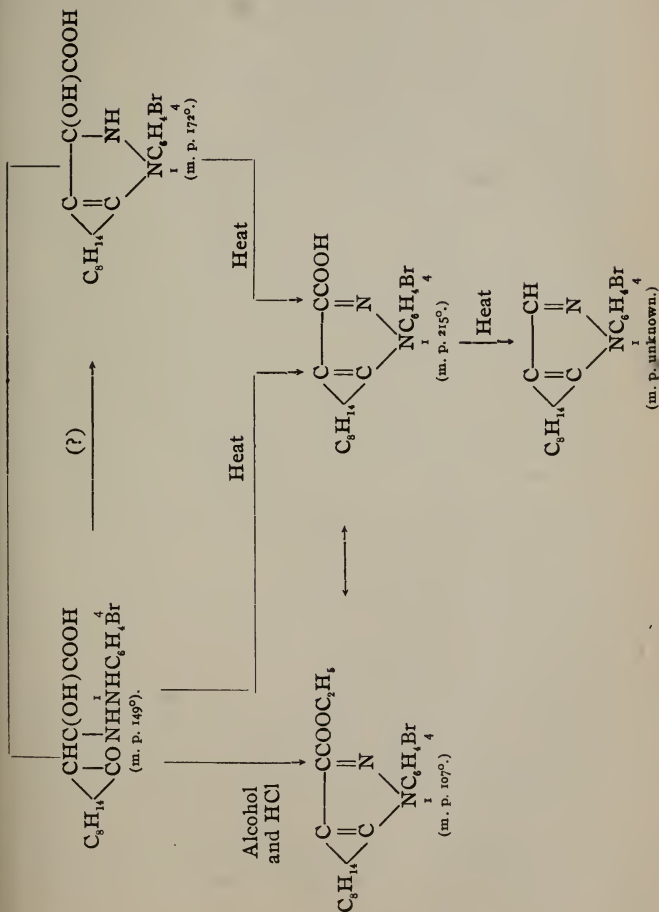
† Identical.

Table I.—Derivatives of Camphoroxalic Acid with (Continued):

PHENYLHYDRAZINE.

Heat
←

* Previously prepared.



paper, J. Bishop Tingle and W. E. Hoffman, Jr.,¹ described two substances obtained by boiling on the water-bath an aqueous-alcoholic solution of semicarbazine hydrochloride (2 mols.), potassium acetate (2 mols.) and camphoroxalic acid (1 mol.). Evaporation of most of the alcohol and the addition of water precipitated a substance which could be crystallized from alcohol and which melted at 200°. It had the same composition as the two compounds referred to above. When this substance was crystallized from glacial acetic acid its melting point was found to be 209°-210°, and it was, therefore, supposed to be identical with the "insoluble compound" described in the earlier paper. In both these papers the experiments were expressly stated to be only of a preliminary nature.

We have made a further investigation of the action of semicarbazine on camphoroxalic acid, in order to try to throw light on this supposed isomerism. First the experiment in which the substances reacted in a closed tube was carried out, and the product treated exactly as described by Bishop Tingle and A. Tingle. After evaporation of the alcohol and acidification of the residue, the precipitate was washed repeatedly with ether and the filtrate extracted three times with fresh portions of the same solvent. The substance left by evaporation of the combined ethereal residues was crystallized twice from acetone, and the material left undissolved by ether was crystallized twice from glacial acetic acid, by the addition of alcohol. The melting-points of these two portions of the reaction product were then compared by determining both simultaneously, in tubes attached to the same thermometer. They melted at exactly the same temperature.

The reaction was next carried out in the manner described by Tingle and Hoffman. Potassium acetate was used to liberate the semicarbazine from its hydrochloride, and the mixed components were boiled on the water-bath until the alcohol was almost entirely evaporated. The crystalline substance, obtained by dilution with water, was recrystallized from alcohol and a part of the recrystallized product was boiled with glacial acetic acid for a few minutes and crystallized by the addition

¹ THIS JOURNAL, 34, 251 (1905).

of alcohol. The two portions, one from alcohol and one from acetic acid, were found to melt at exactly the same temperature when heated simultaneously. Boiling vigorously in glacial acetic acid for half an hour did not change the substance. The compound, when dissolved in potassium carbonate solution and precipitated by acid, appeared in a gelatinous form, but this, when filtered and dried, still melted at the same temperature as before. It was also found that the two substances obtained by the method first described, and the two obtained by this second process, showed identical melting points when any two of them were compared by heating simultaneously in tubes attached to the same thermometer. Furthermore, a mixture of any two of them, when tested in the same manner with each one of the unmixed substances, showed no change in melting point. Samples of the compounds prepared by Bishop Tingle and A. Tingle and by Bishop Tingle and Hoffman were available; therefore the question was further tested by making an exhaustive comparison of these with each other, and with the newly prepared material. With every possible mixture of equal parts of any two of them, the results, in every case, showed that all the preparations were identical.

In the work described above, it was found that the observed melting point varied widely with the rate of heating, and to make accurate comparisons was possible only by attaching 2 capillaries, containing portions of the two substances to be compared, to the thermometer bulb at the same time, and heating them together. The following data on the variation of the melting-point of this semicarbazine derivative were obtained by experiment. In all cases, the capillary containing the substance was placed in the melting point bulb when the thermometer registered 190° , and the heating was begun at once. Capillaries of about the same size were used in all these determinations.

Table II.

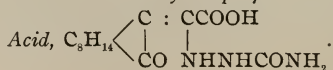
	Rate of rise (above 190°).	Time required.	Observed melting point.
1	2° per minute	5 min. 15 sec.	200°.5
2	4° " "	4 " "	205°.5
3	6° " "	3 " "	208°
4	8° " "	2 " 20 "	209°
5	9° " "	2 " 10 "	209°.5
6	15° " "	1 " 5 "	217°

It was subsequently found that if the substance is heated still more slowly, it melts at 198°; but it will not melt lower than that even with an hour's heating. This must, therefore, be considered the true decomposing temperature of the compound. From the results obtained by Bishop Tingle and A. Tingle,¹ it is evident that an unusual sensitiveness of this compound to slight traces of impurity is a further factor in the variation in melting point.

The substance is rather sparingly soluble in both alcohol and acetone and, when pure, it is practically insoluble in ether. When the crude reaction product is washed with ether, however, the resinous matter which is present appears to render the compound somewhat soluble, which explains why some of it was found in the ethereal washings. The varying data previously recorded in regard to both the solubility and the melting point of this substance are, therefore, satisfactorily explained.

Many other derivatives of camphoroxalic acid, especially those with high melting-points, show a sensitiveness to the rate of heating similar to that described above, though not usually in so marked a degree. The melting points recorded throughout this work are those observed with very slow heating.

The Action of Heat on Carbamylcamphoformeneaminecarboxylic



As stated in the theoretical portion of this paper, at least 3 compounds are formed by heating carbamylcamphoformeneaminecarboxylic acid, *viz.* :

¹ *Loc. cit.*

1. Hydrazodicarbonamide, m. p. 245° .
2. Camphylpyrazolecarboxylic acid, m. p. 255° – 258° .
3. Camphyl-3-keto-1,2,4-heptatriazine, m. p. 305° – 306° .

The experiments were carried out as follows :

The substance was heated in test tubes of 15 mm. diameter, about 3 grams being contained in each. The test tubes were placed in a sulphuric acid-bath in which a thermometer was suspended. It was found that, even when the temperature was raised very slowly, no fusion took place below 198° . After the mass began to fuse the temperature was kept between 196° and 200° , for 20 minutes. Water and carbon dioxide were evolved, neither of them abundantly.

The cooled mass was hard and brittle, with a reddish-brown color and a nitrile-like odor. The odor of camphor was also slightly perceptible. The separation of the products of reaction involved considerable difficulty, but finally the following method was found to be satisfactory :

See Errata p. 644
The powdered mass is treated with cold acetone, filtered and washed repeatedly with acetone. The undissolved portion is then boiled several times with portions of alcohol until the substance still left undissolved is colorless. It is then filtered and washed with alcohol. The white, insoluble substance melts at 235° . The alcohol filtrates are collected and evaporated to crystallization, yielding a yellow substance melting at 305° – 306° . It is purified by boiling with acetone, filtering and washing with acetone. The undissolved material is then recrystallized from alcohol until pure. All the acetone filtrates from the first treatment of the fused material, as well as from the operations just described, are brought together, and the acetone evaporated. A tarry mass remains ; by careful treatment with a small amount of cold acetone, much of the tarry matter can be dissolved, leaving a granular substance which is further purified by filtering and washing with a little acetone. Two or three recrystallizations from acetone give a nearly pure, colorless body, crystallizing in small prisms. When pure, it softens at about 250° , shows marked decomposition at 255° and fuses completely at 258° . More of this

compound can be recovered from the tarry mass by treating it with sodium carbonate solution, filtering and acidifying.

Two of these substances were also obtained when camphor-oxalic acid and semicarbazine were allowed to react at 125° , under pressure. Eight and eight-tenths grams of camphoroxalic acid (1 mol.), 8.8 grams of semicarbazine hydrochloride (2 mols.) and 6.8 grams of potassium hydroxide (3 mols.) were placed in a bomb with 100 cc. of 95 per cent alcohol, and heated for 6 hours, at 124° – 126° . The alcohol was then evaporated and water added. A part of the solid remained undissolved. It was dark from the presence of impurities, but boiling with alcohol removed the color and the compound, being insoluble, was left in nearly pure condition. It was found to be identical with the substance melting at 245° , which was obtained by the fusion of the original semicarbazine derivative. The alcohol solution of the dark impurities was decolorized with animal charcoal, and the alcohol boiled off. A small amount of thick, yellow oil was left which gave a brownish-red color with ferric chloride, in alcoholic solution. It was not further investigated. The aqueous filtrate from the insoluble substance, m. p. 245° , gave, on acidification, a white, finely crystalline substance which softened at 250° and melted at 255° – 258° . It was shown by the mixture test to be identical with the compound of the same melting point which was obtained amongst the products of fusion of the semicarbazine compound.

1. *Hydrazodicarbonamide*.—The compound melting at 245° is soluble in 150–200 parts of boiling water and, on cooling, crystallizes in very thin plates. Two recrystallizations suffice for purification. The substance is insoluble in all the ordinary organic media, and dilute acids and alkalies have no effect upon it. It readily reduces an ammoniacal solution of silver nitrate. Analysis :

I. 0.2290 gram substance gave 0.1705 gram CO_2 and 0.1091 gram H_2O .

II. 0.0933 gram substance gave 37.9 cc. N_2 at 18° and 764 mm.

	Calculated for $C_2H_8O_2N_4$.	Found.
C	20.34	20.30
H	5.12	5.33
N	47.45	47.17

The compound is, undoubtedly, hydrazodicarbonamide, which is formed by heating semicarbazine, elimination of hydrazine taking place.

2. *Camphylpyrazolecarboxylic Acid*.—The substance melting at 255° – 258° is slightly soluble in boiling water, but insoluble in cold. It dissolves in a solution of sodium carbonate and is precipitated by acid, but dissolves in excess of acid. Crystals of the substance are readily soluble in cold, dilute acids, showing that it has basic as well as acidic properties. In alcohol it is extremely soluble, but is readily recrystallized from acetone. The crystals are thick, colorless, prismatic forms, usually aggregated into clusters. Analysis:

I. 0.1844 gram substance gave 0.4478 gram CO_2 and 0.0894 gram H_2O .

II. 0.2330 gram substance gave 0.5615 gram CO_2 and 0.1575 gram H_2O .

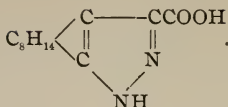
III. 0.1957 gram substance gave 0.4715 gram CO_2 and 0.1387 gram H_2O .

IV. 0.1165 gram substance gave 13.5 cc. N_2 at 25° and 761 mm.

V. 0.1760 gram substance gave 20.1 cc. N_2 at 22° and 755 mm.

	Calculated for $C_{12}H_{18}O_2N_2$.	I.	II.	Found. III.	IV.	V.
C	65.45	66.23	65.73	65.71	. .	. .
H	7.27	6.83	7.56	7.92	. .	. .
N	12.73	. .	. .	. .	12.94	12.83

The same compound was subsequently obtained by the interaction of hydrazine and camphoroxalic acid, and this fact, taken in conjunction with its properties, makes it practically certain that the substance is camphylpyrazolecarboxylic acid,



Its basic properties are attributable to the pyrazole residue.

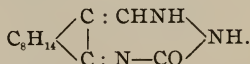
3. *Camphyl-3-keto-1,2,4-heptatriazine*.—The yellow substance, melting at 305°–306°, which was obtained from the fused material, crystallizes from alcohol in small prisms. The compound does not dissolve in a solution of sodium carbonate. It is fairly soluble in alcohol and difficultly soluble in ether, acetone, benzene and ligroin. From 12 grams of the semicarbazine compound, less than 1 gram of this substance was obtained, and this quantity was reduced to only about 250 milligrams in the process of purification. Hence no extensive study of its properties could be made. Analysis :

I. 0.1630 gram substance gave 0.3917 gram CO₂ and 0.1160 gram H₂O.

II. 0.0902 gram substance gave 15.2 cc. N₂ at 19° and 750 mm.

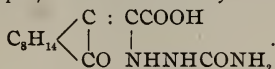
	Calculated for C ₁₂ H ₁₇ ON ₃ .	I.	Found.	II.
C	65.75	65.54		. .
H	7.76	7.96		. .
N	19.18	. .		19.11

The compound has the composition of carbamylcamphoformeneaminecarboxylic acid minus the elements of water and carbon dioxide, and hence is assumed to have the structure represented by the formula



The manner of the formation of these three substances from carbamylcamphoformeneaminecarboxylic acid, by the action of heat, is explained in the theoretical part of this paper (*vide* p. 230).

The Action of Hydrochloric Acid and Alcohol on Carbamyl-
camphoformeneaminecarboxylic Acid,



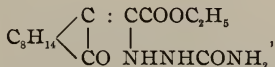
The carbamyl derivative was mixed in a flask with absolute alcohol and dry hydrochloric acid gas was led ^{into} ~~into~~ saturation, the temperature being kept low by immersing the flask in ice-water. A flocculent, white substance began to be formed some time before saturation was reached, and eventually appeared in considerable quantity; but when the saturated solution was allowed to stand, even at 0°, it gradually disappeared.

Some of this flocculent substance was filtered out and purified by recrystallization from acetone. The crystals were colorless, but so small as to be in the form of powder. The compound is readily soluble in hot alcohol, but sparingly in cold. It easily dissolves in ether and chloroform, is sparingly soluble in benzene, and insoluble in ligroin. It does not dissolve in sodium carbonate solution. The substance melts at 191°.

Analysis: 0.0843 gram substance gave 0.1798 gram CO₂ and 0.0597 gram H₂O.

	Calculated for C ₁₆ H ₂₃ O ₄ N ₃ .	Found.
C	58.25	58.17
H	7.44	7.92

The analysis shows the compound to be *ethyl carbamylcamphoformeneaminecarboxylate*,,



which has been previously prepared by Bishop Tingle and A. Tingle, as mentioned in the first part of this paper.

The clear, alcoholic solution, saturated with hydrochloric acid, was poured into a large volume of dilute sodium carbonate solution. An emulsion was formed, but on standing over night the emulsified substance collected into a gummy mass which, when filtered and dried, became hard and granular.

see notes p. 644.

It was found to be extremely soluble in methyl and ethyl alcohol, ether, acetone, chloroform, ethyl acetate and benzene. From solution in all of these liquids it appears as a slightly yellow oil, on evaporation of the solvent at the ordinary temperature. This oil gradually solidifies, requiring sometimes several weeks. From methyl alcohol crystals can be obtained if the solution is kept at 0° . The substance is deposited from ligroin, however, in large, beautiful crystals. They belong to the hemimorphic group of the monoclinic system, for they have a single binary axis of symmetry. The orthopinacoid (100) faces are generally the largest faces on the crystal; the

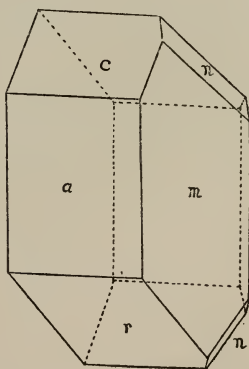


Fig. I.

basal pinacoid (001) and the orthodome (101) are also usually well developed. Two small pyramidal faces, opposite each other with respect to the b axis, are sometimes, but not always to be found, and the presence of these betrays the hemimorphic character of the crystals. The purified compound melts at 91° – 92° . It is insoluble in sodium carbonate solution. Analysis:

I. 0.1620 gram substance gave 0.4001 gram CO_2 and 0.1170 gram H_2O .

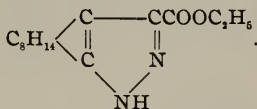
*see errata
p. 644.*

synodone

II. 0.1867 gram substance gave 19.3 cc. N₂ at 16° and 736 mm.

	Calculated for C ₁₄ H ₂₀ O ₂ N ₂ .	Found.
C	67.74	67.36
H	8.06	8.08
N	11.29	11.50

The composition corresponds to that of ethyl camphylpyrazolecarboxylate,



Hydrolysis, effected by warming for a few minutes with potassium hydroxide solution, yielded camphylpyrazolecarboxylic acid (m. p. 255°–258°), proving the substance to be the one formulated above.

When a portion of the alcoholic hydrochloric acid solution was evaporated to dryness, a solid was obtained which crystallizes readily from acetone in colorless needles, softening at 151° and melting at 156°. An alcoholic solution of this substance yields a precipitate of silver chloride when alcoholic silver nitrate is added. By treatment with a solution of sodium carbonate, ethyl camphylpyrazolecarboxylate is liberated (m. p. 91°–92°). This substance is, therefore, *ethyl camphylpyrazolecarboxylate hydrochloride*. The stability of this salt is noteworthy and unusual.

The Action of Urea and of the Methylated Ureas on Camphoroxalic Acid.

Urea.—Five grams of camphoroxalic acid and 2.7 grams of urea (2 mols.) were dissolved in 50 cc. of 95 per cent alcohol. When the mixture was heated in a bomb, at 100°, for 5 hours, no reaction took place, but when heated in the same manner at 135°, for 5 hours, a compound was formed which melts at 192°–194°, with evolution of gas. It was separated from the crude product of the reaction by evaporating the alcohol on the water-bath, and washing the residue with chloroform.

After being recrystallized twice from methyl alcohol it was in a nearly pure condition, though a slight pink color still clung to it. From its solutions it is deposited in an amorphous form, not in definite crystals.

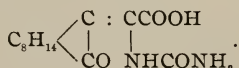
The compound dissolves readily in sodium carbonate solution and is reprecipitated by acidification. Ethyl alcohol dissolves it with ease; acetone, ethyl acetate and chloroform very sparingly; and it is practically insoluble in benzene and ligroin. Analysis:

I. 0.1080 gram substance gave 0.2285 gram CO_2 and 0.0844 gram H_2O .

II. 0.1254 gram substance gave 0.2645 gram CO_2 and 0.0756 gram H_2O .

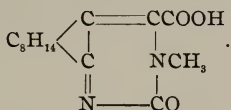
	Calculated for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2$.	I.	Found.	II.
C	58.65	57.71		57.53
H	6.77	8.74		6.74

The low results for carbon are due to a slight defect in the absorption apparatus which was not discovered until after the combustions were completed, and time was not available for the preparation of more of the compound. However, the analysis leaves little doubt that the substance is *formamidyl-camphoformeneaminecarboxylic acid*,



Methylurea.—Methylurea and camphoroxalic acid, in equimolecular proportions, were heated together in a test-tube, at 95° , for 30 minutes. The temperature was then allowed to rise to 105° for a few minutes. Water and carbon dioxide were eliminated. The cooled mass was crystallized from ethyl acetate by the addition of ligroin, and was then purified by further recrystallization from ethyl acetate. The product is a slightly yellow substance which is deposited in elongated, prismatic, translucent crystals, melting at 154° . Small crystals appear quite colorless. The same compound was obtained when equimolecular proportions of methylurea and camphoroxalic acid, in ethyl alcoholic solution, were heated in a bomb

for 5 hours, at 100°. The substance dissolves very slowly in cold, aqueous sodium carbonate, but with gentle warming it goes into solution readily and is precipitated unchanged on acidification. In cold alcohol it is sparingly soluble, but dissolves readily on heating: in ether, acetone and chloroform it is very soluble, but not quite so easily in benzene, and only slightly so in ligroin. Analysis shows that the ketonic and enolic groups of camphoroxalic acid have reacted, the product being *1-methyl-2-keto-4,5-camphylmetadiazine-6-carboxylic acid*,



Analysis :

I. 0.1967 gram substance gave 0.4612 gram CO₂ and 0.1224 gram H₂O.

II. 0.2227 gram substance gave 21.2 cc. N₂ at 15° and 742 mm.

	Calculated for C ₁₄ H ₁₈ O ₃ N ₂ .	I.	Found.	II.
C	64.12	63.95	.	.
H	6.87	6.96	.	.
N	10.69	.	.	10.88

This compound, and also the one from urea, will be investigated more fully at a later date.

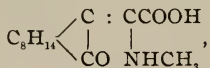
Symmetrical Dimethylurea.—Five grams of camphoroxalic acid (1 mol.) and 4 grams of dimethylurea (2 mols.) were dissolved in 25 cc. of methyl alcohol and heated in a bomb, at 100°–105°, for 5.5 hours. No definite compound could be isolated from the tarry product of the reaction by the use of the ordinary solvents, on account of the extreme solubility of the material. A portion of the mixture, dissolved in alcohol, was poured slowly into sodium carbonate solution, the precipitated tarry matter was filtered out and the clear solution acidified; a small amount of the substance was precipitated which, when dried in the air, melted at 104°–105°. The crude product of the reaction from another experiment, in which the compo-

nents were taken in the same proportion as before, and the conditions of heating were also identical, was worked up as follows: A part of the methyl alcohol was evaporated and the solution poured into aqueous sodium carbonate. The carbonate solution stood over night, and in the morning had the odor of methylamine. After being filtered, it was acidified, and a precipitate appeared of which a part collected in long needles and the remainder in oily drops, that eventually hardened. The substance is extremely soluble in all the ordinary organic media, but can be crystallized from ligroin, separating in long, colorless, prismatic needles which melt at 77° – 78° . The substance gives a brownish-red color with alcoholic ferric chloride. Analysis:

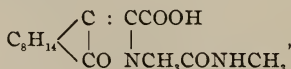
0.1086 gram substance gave 0.2629 gram CO_2 and 0.0787 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{19}\text{O}_3\text{N}$.	Found.
C	65.82	66.02
H	8.01	8.10

It is apparently, therefore, a methylamine derivative, *methylcamphoformeneaminecarboxylic acid*,



which has not been previously prepared. Its origin is, perhaps, due to a decomposition of the dimethylurea, resulting in the formation of methylamine, which then reacted with camphoroxalic acid; or, what seems more probable, in view of the fact that the odor of methylamine appeared only after the product had stood a long time in sodium carbonate solution, a dimethylurea derivative,



was first formed, having the melting point 104° – 105° , and this was hydrolyzed by sodium carbonate into methylamine, car-

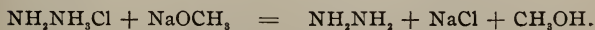
bon dioxide and methylcamphoformeneaminecarboxylic acid. Time was not available for pushing these experiments further, but this matter will also be taken up later, in conjunction with the continuation of the study of the action of urea and methylurea on camphoroxalic acid.

Unsymmetrical Dimethylurea.—Camphoroxalic acid and unsymmetrical dimethylurea, in methyl alcoholic solution, were heated in a bomb, first at 100° – 105° , then, successively, at 125° and at 140° – 145° , in each case for 5 hours. In every experiment the unchanged substances were recovered. After the last heating a very strong odor of dimethylamine was perceptible when the bomb was opened. The experiments were not carried further, as the results gave enough evidence of difference in the action on camphoroxalic acid, of urea and its methyl derivatives to serve our immediate purpose.

The Action of Hydrazine on Camphoroxalic Acid.

A methyl alcoholic solution of hydrazine was prepared by Lobry de Bruyn's method from the hydrochloride, and the strength of the solution approximately determined by means of Fehling's solution. Measured quantities of the solution were then used as desired. For the preparation and titration of the hydrazine solution, we have to thank Mr. W. W. Holland, of this laboratory.

Lobry de Bruyn's directions¹ are not very definite and it may be well, therefore, to state exactly the procedure employed. The quantities given below are convenient and represent suitable proportions of the reacting substances. In a flask fitted with an upright condenser, 100 grams of sodium are added, in small pieces, through the condenser, with the usual precautions, to 150 cc. of absolute methyl alcohol. Forty-two grams (1 mol.) of well pulverized hydrazine hydrochloride are now mixed with the hot mass of sodium methylate (3 mol.). The reaction, which takes place quickly and smoothly, is represented thus :



¹ Rec. Trav. Chim., 13, 433.

After heating a short time, the sodium chloride is filtered out as quickly as possible, with the aid of a suction pump, and the filtrate is distilled from an ordinary fractionating flask. The methyl alcohol which passes off up to about 72° contains only traces of hydrazine. When that temperature is reached the residual, undistilled liquid is placed in a flask to which a Le Bel-Henninge, or similar fractionating apparatus, is attached; it is important to prevent, as far as possible, the hydrazine vapors from coming in contact with the stopper, which should, therefore, be 15–20 cm. above the exit tube. The distillation is then continued under diminished pressure, a manometer being connected with the apparatus. At 30 mm. pressure, the distillate obtained under 50° contained only about 0.5 per cent of hydrazine; between 50° and 60° the fraction contained 2 per cent of the base. The remainder passed over between 60° and 65° , and this solution contained 21 per cent of hydrazine. Throughout the process great care must be taken to avoid unnecessary exposure to the moisture of the air.

Three primary reaction products were obtained by the action of hydrazine on camphoroxalic acid, *viz.*: 1. A compound formed by the action of 1 molecule of hydrazine on 2 of camphoroxalic acid. 2. Hydrazine camphoroxalate. 3. A product resulting from the condensation of 1 molecule of hydrazine with 1 of the acid. The preparation and properties of these substances, in the order mentioned, are described in the succeeding paragraphs.

1. Four grams of camphoroxalic acid were dissolved in the smallest possible amount of methyl alcohol and 3 cc. of a 21 per cent methyl alcoholic solution of hydrazine were added (equimolecular proportions). After standing for 20 hours, the mixture almost completely solidified when it was stirred. The product was recrystallized from methyl alcohol, appearing in the form of long, fine needles which are light yellow in color. It begins to fuse and decompose at about 137° , but complete melting does not take place even at 155° . This crystallized substance was found to contain 2 molecules of methyl alcohol, which are given off slowly at 100° . The compound

obtained by driving off the methyl alcohol is deep yellow in color and decomposes at 150° – 155° , without complete fusion. It dissolves readily in aqueous sodium carbonate solution and is reprecipitated on acidification. With alcoholic ferric chloride it gives a slight, brownish-red color, which soon changes to a yellowish green, due to reduction of the ferric to ferrous chloride. It is so extremely soluble in ethyl alcohol, ether, acetone, ethyl acetate, chloroform and benzene that it cannot be crystallized from them, but is left as a sticky mass by the spontaneous evaporation of any one of these solvents. It is soluble in ligroin with difficulty. The crystals with 2 molecules of methyl alcohol are much less soluble than the alcohol-free material. Analysis :

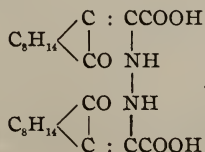
I. 0.3365 gram crystallized substance, when heated at 105° , for 3 hours, lost 0.0395 gram ; for 3 hours longer, 0.0020 gram ; for 2 hours longer, 0.0004 gram. Total loss, 0.0419 gram.

II. 0.2418 gram crystallized substance gave 11.6 cc. N_2 at 11° and 761 mm.

III. 0.1442 gram substance, dried at 100° , gave 0.3432 gram CO_2 and 0.0987 gram H_2O .

	Calculated for $C_{24}H_{32}O_6N_2 \cdot 2CH_3OH$.	I.	Found.	II.
CH_3OH	12.59	12.45		
N	5.51	. .		5.73
	Calculated for $C_{24}H_{32}O_6N_2$.		Found.	
C	64.86		64.91	
H	7.21		7.65	

The compound, which may be termed *biscamphoformene-aminecarboxylic acid*, is formed by the action of 1 molecule of hydrazine on 2 molecules of camphoroxalic acid and, presumably, has the formula

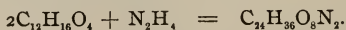


2. In another experiment, 4 grams of camphoroxalic acid, in methyl alcoholic solution, were treated with 6 cc. of 21 per cent solution of hydrazine (2 mols.) in methyl alcohol. In a short time a bulky, yellow precipitate appeared which was found to decompose between 160° and 172° . After recrystallization from hot methyl alcohol, it decomposed at 150° – 155° , and appeared to be identical with the compound described above. The solubilities of the two substances are markedly different. While the one decomposing at the lower temperature is extremely soluble in all of the ordinary solvents, except ligroin, the new substance is only slightly soluble at the ordinary temperature in methyl and ethyl alcohols, acetone, chloroform, ether, benzene and ligroin. It dissolves on warming, but is changed to the lower melting substance. A solution of sodium carbonate quickly dissolves it, but acidification gives a gelatinous precipitate which is readily soluble in the common organic media, and decomposes at 147° – 155° , the change to the other compound having taken place in this process also. This new substance was purified as much as possible by repeated washings with cold alcohol. The purified material is very light yellow in color and begins to decompose at about 186° , complete fusion taking place only at 245° . With alcoholic ferric chloride it gives a slight, brownish-red color, which soon changes to a yellowish-green, due to the production of ferrous chloride. Analysis :

0.1990 gram substance gave 0.4338 gram CO_2 and 0.1375 gram H_2O .

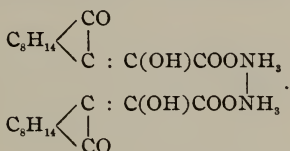
	Calculated for $\text{C}_{24}\text{H}_{36}\text{O}_8\text{N}_2$.	Found.
C	60.00	59.45
H	7.50	7.73

The analysis shows that 1 molecule of hydrazine is combined with 2 of camphoroxalic acid :



On account of its solubility in sodium carbonate solution, it was at first suspected to be formed by the addition of hydrazine to the carbonyl groups, and the change to the other substance

was attributed to the readiness with which water would probably be given off from such an additive compound; it was found, however, that the dried substance, when heated to 160° , for 2 hours, was still unchanged. Further, when a few drops of dilute sulphuric acid were added to a methyl alcoholic solution of the substance, a white, powdery precipitate was formed which was, presumably, hydrazine sulphate. Under similar conditions, the compound decomposing at 150° – 155° was not affected, even after standing 20 hours. It appears, therefore, that the compound is *hydrazine camphoroxalate*,



That it is an unstable salt is shown by the fact that sodium carbonate decomposes it in the cold; and also that, when warmed in the presence of solvents, it dissociates, and the hydrazine liberated reacts with the carbonyl groups.

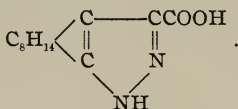
This hydrazine salt was obtained only once. Repeated attempts to prepare it again give only the condensation product.

3. The mother liquors from which the hydrazine salt, or the compound decomposing at 150° – 155° was obtained, gave colorless crystals on standing. When recrystallized from acetone, this substance melted at 255° – 258° . It was also obtained once as the first product when 2 molecules of hydrazine were added to a methyl alcoholic solution of camphoroxalic acid. The compound was observed to be similar in appearance and in melting-point to the acid, $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$, obtained by the fusion of carbamylcamphoformeneaminecarboxylic acid (Cf. p. 259). Comparison of the two showed them to be identical in all respects and a mixture of them melted at the same temperature as each alone. Analysis:

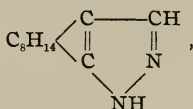
0.1149 gram substance gave 0.2733 gram CO_2 and 0.0793 gram H_2O .

	Calculated for $C_{12}H_{16}O_2N_2$.	Found.
C	65.45	64.87
H	7.27	7.72

As it is formed by the condensation of 1 molecule of camphoroxalic acid with 1 of hydrazine, 2 molecules of water being eliminated, we regard the compound as being camphylpyrazolecarboxylic acid,



In order to obtain, if possible, the simple camphylpyrazole,



some of the acid was subjected to the action of heat. When maintained at 234° for some time, carbon dioxide was evolved copiously and complete fusion eventually took place. The smell of camphor was observed and also a nitrile-like odor. A sublimate of white, prismatic needles, which melted at 217° – 218° , with previous softening, appeared in the upper part of the test-tube containing the material. The cooled mass, which was nearly black, was powdered and washed with hot benzene, which removed most of the color. The residue was recrystallized from alcohol and this treatment repeated, but it failed to remove all of the color and analyses of the product did not give concordant results. The substance separates from alcohol in the form of a fine powder, which darkened at about 275° , but was not fused at 288° . It does not dissolve in sodium carbonate solution. When an alcoholic solution of it is reduced with sodium, and nitric acid and potassium bichromate are added, a beautiful, violet color is produced. This indicates a pyrazole. If the compound is camphylpyrazole, its

high melting point is surprising, as phenylcamphylpyrazole melts at 124° – 125° .¹

Biscamphoformeneaminecarboxylic acid, decomposing at 150° – 155° , was heated at that temperature for 15 or 20 minutes. There was evolution of carbon dioxide and water vapor, and the smell of camphor was perceptible, together with the nitrile-like odor usually observed in heating these compounds. Complete fusion did not take place, but the whole mass appeared to be affected by the decomposition. The cooled product was powdered and treated with hot benzene. A gelatinous mass remained undissolved, which, after being filtered out and dried, became granular and melted at 222° – 223° . The benzene filtrate, when spontaneously evaporated, deposited a gelatinous mass, which was washed with ethyl acetate. The granular solid remaining melted at 232° . The ethyl acetate washings left, on spontaneous evaporation, a red-brown gum in which crystals slowly formed. By washing with small amounts of ethyl acetate these crystals were isolated and then recrystallized from the same solvent. They melted at 221° . When mixed with the above-mentioned substance, melting at 222° – 223° , the mixture melted, not sharply, at 215° , some of the latter compound, which was heated simultaneously in a second capillary tube, melting, as usual, at 222° – 223° . The two compounds have the same color—a light yellow—but the higher-melting one crystallizes from ethyl acetate in fine needles, which aggregate in nodular clusters, while the low-melting one crystallizes from the same solvent in small, translucent prisms.

The compound melting at 222° – 223° is as readily soluble in aqueous sodium carbonate as the substance decomposing at 150° – 155° , and is reprecipitated by the addition of acid. It is very soluble in ethyl and methyl alcohols and acetone, but does not readily dissolve in benzene. After two recrystallizations from ethyl acetate, it was analyzed.

I. 0.1308 gram substance gave 0.3127 gram CO_2 and 0.0895 gram H_2O .

II. 0.0905 gram substance gave 0.2172 gram CO_2 and 0.0623 gram H_2O .

¹ Ann. Chem. (Liebig), 281, 353.

III. 0.1319 gram substance gave 7.6 cc. N_2 at 20° and 740 mm.

	Calculated for		I.	Found.	
	$C_{24}H_{32}O_6N_2$.	$C_{24}H_{30}O_6N_2$.		II.	III.
C	64.86	65.15	65.20	65.45	. .
H	7.21	6.79	7.65	7.70	. .
N	6.30	6.33	. .	. .	6.41

The analyses are scarcely definite enough to enable us to decide with certainty which of the two formulæ belongs to the compound, but the results indicate that it has the composition of the latter. If such be the case, this substance is formed from biscamphoformeneaminecarboxylic acid, $C_{24}H_{32}O_6N_2$, by the loss of 2 atoms of hydrogen.

The substance melting at 232° has a dull yellow color, slightly tinged with red. It readily crystallizes from ethyl acetate. A brick-red deposit usually occurs on the sides of the beaker in which the solution stands; the mother liquors are always red and deposit the same brick-red substance. This colored material appears to be the original substance, mixed with a slight amount of impurity. It melts, not very sharply, at 230° , and mixing with the pure substance raises the melting point close to 232° , the melting point of the pure compound. Recrystallization from ethyl acetate, however, does not remove the color. The compound dissolves very readily in a solution of sodium carbonate, disappearing instantly. Acidification precipitates it unchanged, m. p. 225° – 227° . Alcohol, ether and acetone dissolve it with extreme readiness, and in benzene it is moderately soluble, but is very sparingly so in ligroin. The specimen analyzed had been recrystallized twice from ethyl acetate. Analysis:

0.1354 gram substance gave 0.3236 gram CO_2 and 0.0914 gram H_2O .

	Calculated for $C_{24}H_{30}O_6N_2$.	Found.
C	65.15	65.18
H	6.79	7.55

The compound appears, therefore, to be isomeric with that melting at 222° – 223° . Further work must be done before

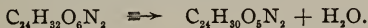
anything can be said with assurance concerning the structure of the two, and even their composition should be tested by additional analyses.

The substance melting at 221° was recrystallized from ethyl acetate and analyzed.

0.0992 gram substance gave 0.2458 gram CO_2 and 0.0662 gram H_2O .

	Calculated for $\text{C}_{24}\text{H}_{30}\text{O}_5\text{N}_2$.	Found.
C	67.66	67.58
H	7.04	7.46

The analysis indicates that the compound is an anhydride of biscamphoformeneaminecarboxylic acid.



Various formulas for such a substance are discussed on page 239. It was impossible to make an extended study of this compound on account of the small quantity of material available; indeed the analysis itself should not be accepted without confirmation, on account of the difficulty of determining the degree of purity attained with so small a quantity of the substance. The investigation of these bodies will be continued in this laboratory.

The Action of Phenylhydrazine on Camphoroxalic Acid.

As mentioned on page 240, the following derivatives of phenylhydrazine and camphoroxalic acid had been prepared before this investigation was commenced: 1. Phenylhydrazine camphoroxalate (?). 2. Ethyl camphoroxalate phenylhydrazide, and the corresponding methyl ester. 3. Ethyl and methyl camphylphenylpyrazolecarboxylate. 4. Camphylphenylpyrazolecarboxylic acid, by the hydrolysis of the esters. We have now obtained an addition compound and have prepared the last-named of the above substances (number 4) directly from camphoroxalic acid, but we have failed in our efforts to prepare phenylhydrazine camphoroxalate.

The Addition Compound.—To camphoroxalic acid (1 mol.) in chloroform solution, phenylhydrazine (2 mols.) was added. In a few minutes the mixture suddenly solidified, the substance

formed having a light yellow color and melting at 120° , with decomposition. It was recrystallized from boiling chloroform. The crystals are long and very fine needles, which are somewhat difficult to manipulate on account of their lightness. The compound is easily dissolved by aqueous sodium carbonate, and acidification reprecipitates it. It is readily soluble in alcohol, ether, chloroform and benzene; sparingly soluble in ligroin, and may be recrystallized from hot benzene as well as from chloroform. From these two solvents it sometimes separates as a transparent, gelatinous mass instead of in crystals. With alcoholic ferric chloride a slight brown color is formed; the addition of concentrated nitric acid causes a violent reaction and the production of an intense, reddish-violet color.

The same substance is obtained when phenylhydrazine reacts, at the ordinary temperature, with camphoroxalic acid in alcohol, ether, or benzene solution. It is also formed when the acid (1 mol.), in alcoholic solution, is neutralized with potassium carbonate and treated with phenylhydrazine (1 mol.). Dilution with water and acidification with acetic acid precipitated the yellow compound, melting at 120° . Five grams of camphoroxalic acid and 2.4 grams phenylhydrazine gave 7.4 grams of the substance. Analysis:

I. 0.2367 gram substance gave 0.5602 gram CO_2 and 0.1495 gram H_2O .

II. 0.2559 gram substance gave 0.6043 gram CO_2 and 0.1644 gram H_2O .

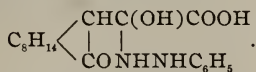
III. 0.1910 gram substance gave 14.7 cc. N_2 at 19° and 747 mm.

IV. 0.1970 gram substance gave 15.6 cc. N_2 at 20° and 746 mm.

	Calculated for $\text{C}_{18}\text{H}_{24}\text{O}_4\text{N}_2$.	I.	II.	Found. III.	IV.
C	65.12	64.55	64.41	. .	. .
H	7.28	7.07	7.19	. .	. .
N	8.49	. .	. .	8.69	8.88

The analysis shows that the substance is an addition compound of camphoroxalic acid and phenylhydrazine, and its formation from potassium camphoroxalate excludes the possi-

bility of its being a phenylhydrazine salt of the acid. It must, therefore, be represented by the formula



In the hope of eliminating a molecule of water, some of this compound was placed in a vacuum desiccator containing sulphuric acid, and allowed to stand for 2 months. No change took place. This, and the further fact that its solutions can be boiled, distinguish the substance from the very unstable additive compounds of phenylhydrazine with ketones which have been isolated. This point has been discussed more fully in the theoretical part (*vide* p. 241).

The chloroform mother-liquor, containing the excess of phenylhydrazine from the reaction described above, if allowed to stand a few days at ordinary temperatures, deposited the characteristic, glistening, flaky crystals of phenylhydrazine hydrochloride. The substance was identified by the fact that it gives a precipitate of silver chloride when treated, in alcoholic solution, with silver nitrate; and when aqueous alkali comes in contact with it, phenylhydrazine is liberated.

The purified hydrochloride was found to melt at 233° , with previous darkening, if heated at a slow rate, instead of 240° as given by Broche,¹ or 240° – 243° as given by Autenreith.² The decomposition of chloroform by phenylhydrazine, with the formation of phenylhydrazine hydrochloride, has been previously noted and investigated by Brunner and his co-workers.³

After removal of the phenylhydrazine hydrochloride from the chloroform mother-liquor, it deposited, on standing at the ordinary temperature, a small amount of a substance melting at 196° . When the compound melting at 120° was boiled for 15 or 20 minutes, in alcoholic solution, or when it was heated to fusion without a solvent, the same substance was obtained in relatively large quantity. The latter reaction takes place at 90° – 100° if this temperature is maintained for several hours;

¹ J. prakt. Chem., [2], 50, 114.

² Ber. d. chem. Ges., 29, 1656.

³ *Ibid.*, 30, 2587 (1897); 31, 1406 (1898).

complete fusion occurs, with elimination of water. The substance in question was also formed when camphoroxalic acid was heated with 1, 2 or 3 molecules of phenylhydrazine at 95° – 100° , water and a small amount of carbon dioxide being given off in each case. In all these experiments the product was purified by crystallization from alcohol, it being sparingly soluble in cold alcohol and readily in hot. It dissolves very quickly in chloroform, less easily in ether, is readily soluble in benzene and almost insoluble in ligroin. It can be crystallized from benzene as well as from alcohol. Cold, aqueous potassium carbonate dissolves the substance slowly, but on warming a solution is formed quickly, with effervescence. Acidification reprecipitates the substance unchanged.

The crystals deposited from alcoholic solutions were found to have 1 molecule of alcohol of crystallization. Beautiful, colorless crystals were readily obtained which were frequently 5 mm. long and sometimes had a length of 1 cm. They are monoclinic in form, with normal symmetry, *i. e.*, 1 plane and 1 axis of symmetry. The faces observed to be most strongly developed were the basal pinacoid (001), the orthopinacoid

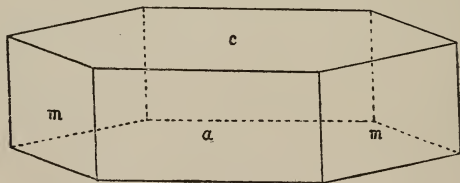


Fig. II.

(100) and the unit prism (110). Orthodome and unit pyramid faces were frequently noticed, but were not well developed. The crystals are flattened parallel to the *b* axis, and present a tubular appearance, as shown in Fig. II. They soon lose their luster, even when kept in closed vessels. The melting-point of the air-dried crystals is not different from that of the substance after expulsion of the alcohol of crystallization. Analysis of the substance dried in a desiccator :

I. 0.2342 gram substance gave 0.5985 gram CO_2 and 0.1606 gram H_2O .

II. 0.2094 gram substance gave 14.2 cc. N_2 at 19° and 765 mm.

III. 0.2190 gram substance gave 14.85 cc. N_2 at 18° and 766 mm.

IV. 0.1468 gram substance, heated in an air-bath for 3 hours, at 125° – 135° , lost 0.0179 gram.

	Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2, \text{C}_2\text{H}_5\text{OH}$.	I.	Found.		
			II.	III.	IV.
C	70.12	69.70	. .	. .	. .
H	7.65	7.67	. .	. .	. .
N	8.20	. .	7.85	7.90	. .
$\text{C}_2\text{H}_5\text{OH}$	13.45	. .	. .	. .	12.17

Analysis of the substance dried at 125° :

I. 0.2075 gram substance gave 0.5534 gram CO_2 and 0.1302 gram H_2O .

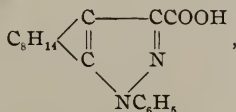
II. 0.1721 gram substance gave 0.4596 gram CO_2 and 0.1085 gram H_2O . *see errata p. 644*

III. 0.2646 gram substance gave 21.8 cc. N_2 at 21° and 755 mm.

IV. 0.2687 gram substance gave 22.7 cc. N_2 at 24° and 748 mm.

	Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$.	I.	Found.		
			II.	III.	IV.
C	72.92	72.72	72.86	. .	. .
H	6.80	7.02	7.05	. .	. .
N	9.47	. .	. .	9.32	9.32

The compound is evidently camphylphenylpyrazolecarboxylic acid,



which was previously made by J. Bishop Tingle¹ by hydrolyzing the ethyl ester, the latter being formed from the phenylhydrazide of ethylcamphoroxalate by the action of heat, by

¹ THIS JOURNAL, 19, 405.

the dehydrating action of hot glacial acetic acid, or of hydrochloric acid, in alcoholic solution. He found that the substance crystallizes from benzene with 0.5 molecule of benzene of crystallization. He also mentions that the acid gives no color with concentrated nitric acid, while the ester gives a pale yellow color. We find that if the solution of the acid, in concentrated nitric acid, is very gently warmed, this pale yellow color appears. An alcoholic solution of ferric chloride gives, with the acid, a red color bordering on orange.

An attempt to make camphylphenylpyrazole carboxylic acid by condensing phenylhydrazine and camphoroxalic acid, in benzene solution, in the presence of fused calcium chloride, did not proceed satisfactorily. The addition compound, melting at 120° , was first formed. The products of the reaction were boiled on a water-bath, in a flask with a return condenser, until this addition compound disappeared, which required several hours. Considerable quantities of phenylhydrazine hydrochloride separated out, the hydrochloric acid doubtless being liberated by the formation of calcium salts of camphoroxalic acid and the acids derived from it by the action of phenylhydrazine. The benzene filtrate from the hydrochloride and the calcium chloride was evaporated to dryness, the residual mass dissolved in alcohol, and the solution poured into a solution of potassium carbonate. Dilution with water and acidification precipitated a small amount of camphylphenylpyrazolecarboxylic acid. No other products of the reaction were found.

J. Bishop Tingle¹ has described a compound, melting at 214° – 215° with previous darkening, which he obtained when camphoroxalic acid and 2 molecules of phenylhydrazine, in anhydrous ethereal solution, were boiled for 2 hours in an apparatus with a return condenser. This compound was supposed to be phenylhydrazine camphoroxalate, but was not analyzed. Attempts were made to obtain the substance again for further study, but when the ethereal solutions of camphoroxalic acid and phenylhydrazine were poured together, the addition com-

¹ THIS JOURNAL, 20, 328 (1898).

pound, m. p. 120° , was at once formed, the whole mass solidifying and the ether boiling with the heat of the reaction.

Boiling on the water-bath, with a return condenser, for 3 hours, produced no change in the mass, even when more ether was added. The experiment was repeated, both with ordinary ether and with ether dried over sodium, with the same result. Attempts to get the phenylhydrazine salt of camphylphenylpyrazolecarboxylic acid, by treating the acid with excess of phenylhydrazine, were likewise unavailing.

The Action of Parabromphenylhydrazine on Camphoroxalic Acid.

The compounds obtained by the action of parabromphenylhydrazine on camphoroxalic acid correspond fully to those obtained with phenylhydrazine, with the exception of one substance, which has the composition of the addition compound minus 1 molecule of water. Such a body was not obtained in the phenylhydrazine series.

Two compounds, which melt at 149° and 172° , respectively, are formed whenever camphoroxalic acid and parabromphenylhydrazine are brought together in alcoholic solution. What experimental factors determine which shall be produced in larger quantity were not learned. Under seemingly similar conditions, sometimes one and sometimes the other separates first, and in one experiment the two separated at the same time, each in its characteristic crystalline form. When crystals of one substance have been separated and completely removed from the solution, the mother-liquor usually next deposits crystals of the other compound. The length of heating is not the determining factor, for either may be obtained without any heating at all. Although the substance melting at 172° was first obtained by evaporating the solution to a small volume and allowing it to stand, the other compound separated first in another experiment in which the substances, in absolute alcoholic solution, were boiled in a flask with a return condenser for an hour and a half, the solution being evaporated to a small volume and allowed to stand. It is possible that the concentration of the parabromphenylhydrazine may determine the relative amounts of the two compounds, because it was

observed that with a small volume of solvent, and a large excess of this substance, more of the low-melting, additive compound was obtained. The method of procedure given in the succeeding detailed description of the experiments is the one employed when these two substances were obtained for the first time. Repetition of the experiments may or may not give the same results.

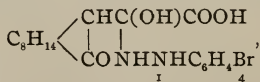
Two and one-half grams of camphoroxalic acid (1 mol.) and 4 grams parabromphenylhydrazine were dissolved in a small amount of alcohol and the solution warmed for a few minutes. The reaction mixture then solidified rather suddenly into a yellow mass. The substance was filtered and recrystallized from alcohol. It forms very slender, yellow needles, which melt at 149° with evolution of gas. The compound is readily soluble in methyl and ethyl alcohols, extremely soluble in acetone and chloroform, fairly so in ether and benzene, but is soluble with difficulty in ligroin. From alcohol or benzene solution it sometimes separates out as a transparent, gelatinous mass. It dissolves readily in aqueous sodium carbonate and is reprecipitated by acidification. With ferric chloride, in alcoholic solution, only a slight brownish color is produced. Concentrated nitric acid attacks it violently, with the formation of a deep red color. Analysis :

I. 0.2409 gram substance gave 0.4603 gram CO_2 and 0.1150 gram H_2O .

II. 0.1801 gram substance gave 0.0786 gram AgBr.

	Calculated for $\text{C}_{18}\text{H}_{23}\text{O}_4\text{N}_2\text{Br}$.	I.	Found.	II.
C	52.53	52.14		. .
H	5.63	5.34		. .
Br	19.46	. .		18.57

The analysis shows it to be an *addition compound*,



corresponding to that formed with phenylhydrazine, m. p. 120° , which it resembles in appearance and behavior. In order to test its stability, it was boiled for 2 hours with abso-

lute alcohol, but it remained unchanged. The same point was further proved by the fact that the compound, when warmed with acetic anhydride to about 75° , for an hour, was precipitated unchanged on dilution with water. Such behavior, as pointed out in the earlier portion of this paper, is a strong argument against the substance being a ketone additive compound, of the usual type ascribed to such substances.

Carbon and hydrogen in this compound, and in the others containing bromine which are described subsequently, were determined in the presence of copper oxide, by the method recently worked out by one of us.¹

Seven and one-half grams of camphoroxalic acid and 6.5 grams (1 mol.) of parabromophenylhydrazine were dissolved in alcohol and boiled on the water-bath to a small volume. On standing over night, crystals were deposited which melt at 172° , with evolution of gas. The substance may be recrystallized readily from alcohol. Very perfect, though not large, crystals are formed which belong to the orthorhombic system. The macrodome (101) and brachydome (011) forms are strongly developed, and the crystals frequently approach the octohedron in shape, but are usually elongated somewhat in the *c* axis. The macropinacoid form (100) is often present as a small face. The crystals are not colorless even after repeated crystallizations, but have a slight brownish tinge. In recrystallizing the substance, crystals of a different kind were sometimes deposited in very small amount. These were light-yellow colored needles, aggregated in fan-like clusters, and were not lustrous like the other variety. They melted at the same temperature, 172° , as the orthorhombic crystals, but were obtained in too small amount for further comparison. The substance is very soluble in ether, acetone and chloroform; readily in methyl and ethyl alcohols; sparingly in benzene; and soluble with difficulty in ligroin. It does not dissolve in aqueous sodium carbonate, even on boiling, and warm alkali hydroxide solution does not dissolve it, but slowly effects hy-

¹ C. J. Robinson: THIS JOURNAL, **35**, 531 (1906).

see errata
p. 822.

drolysis. It is soluble in alcoholic alkali hydroxide, but rapid decomposition takes place, with the formation of a red color, probably due to free parabromophenylhydrazine. However, if an alcoholic solution of the compound is poured into a solution of sodium carbonate it is not precipitated by the addition of water, but comes down unchanged, m. p. 169° , on acidification. Its extreme insolubility in water presumably prevents its going into solution in aqueous alkali.

An alcoholic solution of ferric chloride gives, with this substance, a peculiar, dull brownish-red color, and the addition of water causes a blue fluorescence. Analysis:

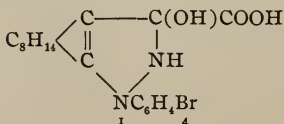
I. 0.2135 gram substance gave 0.4308 gram CO_2 and 0.0982 gram H_2O .

II. 0.2624 gram substance gave 16.2 cc. N_2 at 19° and 758 mm.

	Calculated for $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}_2\text{Br}$.	I.	Found.	II.
C	54.94	55.03		. .
H	5.38	5.15		. .
N	7.14	. .		7.08

The crystallized substance did not change in weight when heated at 110° , for 2 hours.

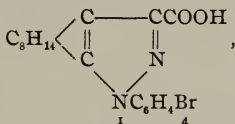
This compound has the same composition as the addition product, melting at 149° , minus 1 molecule of water. The latter is attacked by concentrated nitric acid with almost explosive violence, while the present substance, when treated with the same reagent, goes into solution slowly and quietly, and a pale yellow color is developed. In this respect, as well as in its crystallizing power, it is analogous to camphylphenylpyrazolecarboxylic acid. Hence it seems probable that the compound melting at 172° contains the pyrazole ring, although only 1 molecule of water has been eliminated. As stated in the theoretical part,



seems the preferable one of the three formulæ possible for such a substance.

An attempt was made to acetylate the compound melting at 172° by the action of acetic anhydride. When heated with the anhydride alone, the substance did not dissolve, but on the addition of a few drops of concentrated sulphuric acid, solution took place at once, however, only a tarry mass was formed from which no definite product could be isolated.

Camphylparabromophenylpyrazolecarboxylic acid,



was obtained by the action of heat on either of the two compounds described above. A quantity of the addition compound, which had not been completely purified, was placed in a test-tube and heated in a sulphuric-acid bath, the temperature being raised slowly. At 110° it began to give off water, and partial fusion took place, but eventually the entire mass became solid again and further heating to 135° gave no action except the elimination of a small quantity of carbon dioxide. The cooled mass was brown and brittle. It was powdered and dissolved in boiling benzene. On cooling, a colorless substance was deposited which melts at 215° when heated slowly. The procedure with the compound melting at 172° was similar. It began to decompose after heating for some time at 155° , and partial fusion took place, with the elimination of water. After a few minutes the material again became solid. The cooled mass was treated in the same way as in the case of the addition compound, and the two products were found to be identical.

This new compound dissolves slowly in cold sodium carbonate solution, but readily when warmed. Acidification reprecipitates it. It crystallizes from benzene or alcohol in clusters of small needles, the clusters often being nodular in appearance. It is readily soluble in ether, acetone, chloroform and ethyl acetate, but is almost insoluble in ligroin. Analysis:

0.1937 gram substance gave 0.4095 gram CO_2 and 0.0923 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}$.	Found.
C	57.58	57.66
H	5.10	5.33

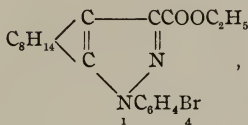
The analysis shows it to be *camphylparabromphenylpyrazolecarboxylic acid*, with the formula given above.

Ethyl camphylparabromphenylpyrazolecarboxylate was obtained by the action of absolute alcohol and hydrochloric acid on the addition compound, m. p. 149° . The latter substance was dissolved in absolute alcohol, and the solution saturated with dry hydrochloric acid gas, the liquid being cooled with ice-water. After standing 2 days, the mixture was poured into water. A slightly yellow substance was precipitated which was filtered, dried and found to melt at 105° . No further precipitate was produced by neutralizing the filtrate with sodium carbonate. To remove any acid that might be present in the precipitated substance it was dissolved in alcohol, the solution was treated with dry sodium carbonate and allowed to stand for several hours. The liquid was then filtered, and the filtrate poured into water. An emulsion was formed which, after the addition of sodium chloride, was extracted with ether. Evaporation of the ether left an oily substance which was readily crystallized from acetone, and purified by recrystallization from the same solvent. Magnificent crystals were formed, which always appeared somewhat yellow, though translucent, but were colorless when powdered. Some of the crystals were nearly 1 cm. in length. They belong to the triclinic system and, apparently, to the asymmetric group of that system. The pure compound melts at 107° . It does not dissolve in sodium carbonate, and gives no color with ferric chloride. It is extremely soluble in chloroform and benzene, very soluble in ether and acetone, readily in alcohol, and slightly in ligroin. Dilute sulphuric acid does not dissolve it, even in 50 per cent alcoholic solution. Analysis:

0.2125 gram substance gave 0.4624 gram CO_2 and 0.1045 gram H_2O .

	Calculated for $C_{20}H_{23}O_2N_2Br$.	Found.
C	59.52	59.35
H	5.75	5.50

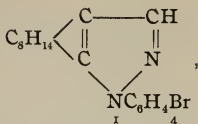
The substance is, therefore, *ethyl camphylparabromphenylpyrazolecarboxylate*,



which is formed from the addition compound by a condensation involving the loss of two molecules of water, and the formation of a pyrazole ring, esterification taking place also. The fact that it does not dissolve in acid shows that it is only very slightly basic, if at all. In contrast with this compound, ethyl camphylpyrazolecarboxylate forms a stable salt with hydrochloric acid (Cf. p. 233).

An attempt to prepare camphylpyrazolecarboxylic acid from camphylparabromphenylpyrazolecarboxylic acid, by oxidizing away the bromphenyl group, was not successful. The experiment was carried out with potassium permanganate, in boiling acetone solution, but the original substance was recovered unchanged.

What appears to be *camphylparabromphenylpyrazole* was obtained from the carboxylic acid by the action of heat. The acid fuses at 215° , and it was maintained at 215° – 218° until evolution of carbon dioxide ceased, which required about an hour for 3.5 grams. The cooled mass was vitreous, very lustrous and appeared black, but in small pieces it was only slightly brown, and was nearly transparent. It was found to be extremely soluble in all the ordinary organic solvents, including ligroin, and was left as an oily residue on spontaneous evaporation. On this account, we were unable to purify the small quantity of the substance which we had at our disposal and, therefore, no analysis was obtained. It is, without much doubt, camphylparabromphenylpyrazole,



because the analogous compound, camphylphenylpyrazole, is described by Bishop, Claisen and Sinclair¹ as having similar properties, and being very difficult to crystallize.

The Hydration Product of Camphoroxalic Acid.

Some years ago, Bishop Tingle² found that when camphoroxalic acid is heated with dilute, aqueous hydrochloric or sulphuric acid, a product is formed which gives an intense blue color with alcoholic ferric chloride solution, and has the composition of camphoroxalic acid plus 2 molecules of water. A further investigation of this substance was undertaken to determine, if possible, its structure, but on account of the extreme instability of the compound, the study has not yet been carried very far, but will, it is hoped, be taken up at a future date.

The substance was prepared as described by Bishop Tingle, by heating 6 grams of camphoroxalic acid with 25 cc. of 1 : 3 sulphuric acid, in a closed tube, at 135°–140°, for 9 to 10 hours. Variations in the concentration of the acid and in the temperature showed that the best results were obtained under the conditions described. The product had the horny appearance mentioned in the previous work, but crystals were observed only when the tubes were well filled, and the pressure, consequently, high. The yield was also improved by a high pressure. It appears to be best to fill the tubes nearly two-thirds full. The product has an aromatic odor, suggestive of fresh pine. It was purified by extracting in a Soxhlet apparatus with low-boiling ligroin, until the substance remaining in the extraction apparatus gives a pure blue color with alcoholic ferric chloride solution; this substance is then recrystallized from chloroform by the addition of ligroin. Temperatures above 60° must be avoided, as the compound reverts with the utmost readiness to camphoroxalic acid, therefore, the ligroin used for this extraction should

¹ Ann. Chem. (Liebig), **281**, 353.

² THIS JOURNAL, **20**, 329 (1898).

boil below 60° , and solutions of the substance should not be warmed. It crystallizes with difficulty in nodular forms, which melt at 92° . The color reaction with ferric chloride is not instantaneous; first a yellow color appears, which changes gradually, through green, to a rich blue. Addition of water to the colored, alcoholic solution converts it to a bluish-violet. Analysis of the substance gave results agreeing with those obtained by Bishop Tingle.

The acid liquid from the tubes in which the reaction takes place contains some of the product, which can be recovered by extraction with ether. This liquid, before extraction with ether, has a strong odor like that of pine, as described above. When warmed, it gives up a small amount of carbon dioxide.

The hydration product yielded no salt when treated with barium chloride, but with barium hydroxide a salt was obtained which is readily soluble in water, fairly soluble in 50 per cent alcohol, but insoluble in absolute alcohol even on boiling. It was not analyzed. When the hydrated acid was treated carefully with aqueous sodium carbonate, of known strength, till litmus paper showed neutrality, 4 equivalents of the carbonate were required, indicating the tetrabascity of the acid. This was only an approximate determination.

When dissolved in chloroform, in the presence of 2 mols. of aniline, the substance yields, at the ordinary temperature, a compound melting at 158° , which is, apparently, identical with the product obtained under similar circumstances with camphoroxalic acid. The sodium salt, in aqueous solution, at room temperature, yields a compound with semicarbazine which melts at 200° and is identical with the substance obtained with camphoroxalic acid.

To an aqueous solution of the sodium salt there was added a solution of 2 molecules of hydroxylamine, obtained from the hydrochloride by the use of sodium carbonate; the mixture was allowed to remain for several days without heating. A colorless product is formed which is not precipitated by acidification, but can be extracted with ether. It melts, with decomposition, at 181° – 182° . No product of hydroxylamine

with camphoroxalic acid is known which has such a melting point. On account of the difficulty of preparing pure material in quantity, these investigations were not carried further.

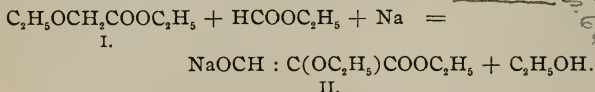
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contributions from the Sheffield Laboratory of Yale University.

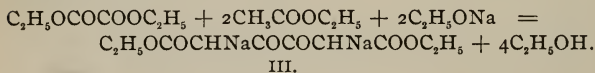
CXXXIV. — RESEARCHES ON FURFURANS: ON
2,5-DICARBETHOXY-3,4-DIKETOTETRA-
HYDROFURFURAN. I.

BY TREAT B. JOHNSON AND CARL O. JOHNS.

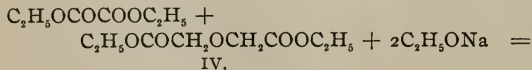
In a recent publication from this laboratory, Johnson and McCollum¹ have shown that ethyl formate condenses with diethyl glycollate, I., in the presence of metallic sodium, to form the sodium salt of ethyl α -ethoxy- β -hydroxyacrylate, II. :



It has also been observed by Wislicenus² that diethyl oxalate can condense with 2 molecular proportions of ethyl acetate, in the presence of sodium ethylate, to form the disodium salt of diethyl ketipate, III. :

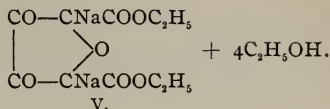


It seemed probable to the writers that diethyl oxalate might condense with diethyl diglycollate, IV., to form the disodium salt of 2,5-dicarbethoxy-3,4-diketotetrahydrofurfuran, V. We find that this condensation takes place in the normal manner, according to the following equation :

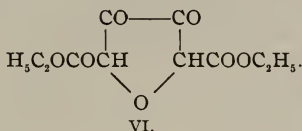


¹ J. Biol. Chem., 1, 437.

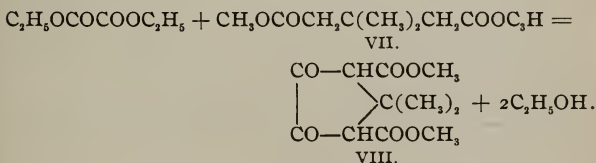
² Ber. d. chem. Ges., 20, 591. Ann. Chem. (Liebig), 246, 328.



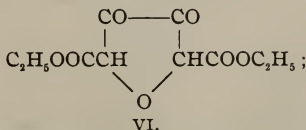
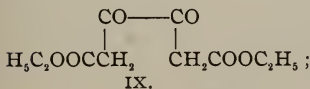
When this salt, V., was treated with acids a crystalline ester, VI., was obtained.



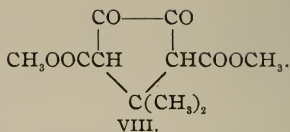
This condensation is analogous to that described by Komppa.¹ He found that diethyl oxalate condensed with dimethyl β,β -dimethylglutarate, VII., to give the dimethyl diketoapocamphorate, VIII. :



The relationship between diethyl ketipate, IX., 2,5-dicarbethoxy-3,4-diketotetrahydrofurfuran, VI., and dimethyl diketoapocamphorate, VIII., is illustrated by the following formulas :

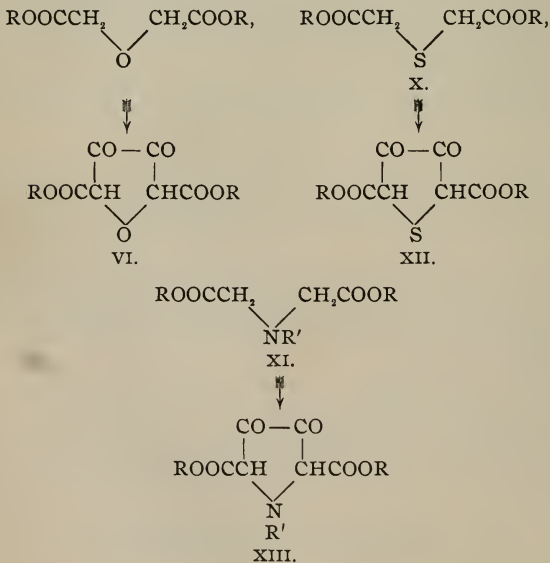


¹ Ber. d. chem. Ges., **32**, 1421; **34**, 2472; **36**, 4332. Dieckmann : *Ibid.*, **32**, 1933.



2,5-Dicarbethoxy-3,4-diketotetrahydrofurfuran, VI., is a representative of a new class of ketonic tetrahydrofurfurans. The study of derivatives of this interesting body is in progress in this laboratory.

We shall also attempt to condense diethyl oxalate with esters of thiodiglycolic acid, X., and nitrogen substituted iminodiacetic acids, XI.



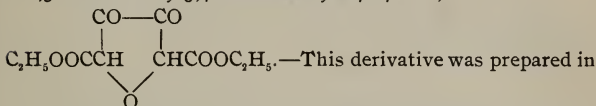
2,5-Dicarbethoxy-3,4-diketotetrahydrothiophene, XII., would be a representative of the unknown series of tetrahydro-

thiophanes. The term "thiophane" is ascribed by Mabery¹ to this new class of compounds. This series is of interest since Mabery's² investigations seem to indicate that tetrahydrothiophenes are present in the sulphur oils of Canadian petroleum.

EXPERIMENTAL.

The diglycollic acid that was used in this work was prepared according to directions given by Lossen.³

2,5-Dicarbethoxy-3,4-diketotetrahydrofurfuran,



the following manner: The calculated quantity of sodium ethylate was obtained by digesting 4 grams of metallic sodium and 8 grams of absolute alcohol in ether, until the sodium disappeared. A mixture of 11.5 grams of diethyl oxalate and 15 grams of diethyl diglycollate were then slowly added to the ether solution. There was an immediate reaction and sufficient heat was evolved to cause the ether to boil. A yellow sodium salt deposited on cooling. The mixture was allowed to stand about 5 days, when the salt was filtered off and dried in the air. The yield of salt was practically quantitative. When an aqueous solution of this salt was acidified with dilute sulphuric acid a colorless, crystalline deposit was obtained. The compound was very soluble in hot alcohol. It deposited, on cooling, in stout, prismatic crystals that melted at 189°, without effervescence, to a clear oil. Analysis:

0.2900 gram substance gave 0.5207 gram CO₂ and 0.1387 gram H₂O.

	Calculated for C ₁₀ H ₁₂ O ₇ .	Found.
C	49.18	48.97
H	4.92	5.3

¹ THIS JOURNAL, 35, 404.

² *Loc. cit.*

³ Ann. Chem. (Liebig), 342, 121 (1905).

Sodium Salt of 2,5-Dicarbethoxy-3,4-diketotetrahydrofurfuran.
—This salt was prepared for analysis by dissolving 1 gram of the furfuran derivative in alcohol containing 2 molecular proportions of sodium ethylate. The salt deposited as a white, microscopic powder. A sodium determination gave the following result :

0.1012 gram salt gave 0.0512 gram Na_2SO_4 .

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_7\text{Na}_2$.	Found.
Na	15.97	16.3

NEW HAVEN, CONN.,
June 5, 1906.

Contributions from the Sheffield Laboratory of Yale University.

CXXXV.—ORTHO-, META- AND PARAIODHIPPURIC ACIDS.

BY TREAT B. JOHNSON AND HAROLD A. MEADE.

The object of the work described in this paper was to synthesize ortho-, meta- and paraiodhippuric acids. We shall also describe some new derivatives of 3,5-dinitrobenzoic acid.

Our interest in iodhippuric acids was incited by a recent paper—"Ueber den physiologischen Abbau von Iodalalbumin"—by Mosse and Neuberg,¹ in which the authors have described some interesting end products of the metabolism of iodine-albumin² when fed to dogs and rabbits. They isolated from the blood of dogs an iodine derivative that was identified as orthiodobenzoic acid, "the melting point of which corresponded to that given for the ortho acid, 156°–157°, by Kekulé.³ Wachter⁴ has shown that this acid melts at 162°." From the urine of rabbits they separated the barium salt of a new, iodine substituted acid. Their analytical determinations agreed with the calculated values for a salt of iodhippuric acid. This acid was not obtained in a pure condition. They concluded, nevertheless, that they were dealing with an ortho de-

¹ Z. physiol. Chem., 37, 427 (1903). *see errata p. 644.*

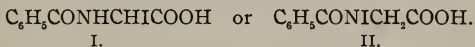
² "Zu die Untersuchungen, diente ein technisches Product, das lösliche Iodeigon-natrium von der chemischen Fabrik Helfenberg in Sachsen (Mosse and Neuberg)."

³ Ber. d. chem. Ges., 7, 1007 (1874).

⁴ *Ibid.*, 26, 1744 (1893).

rivative because it was converted into glycocoll and orthoiodbenzoic acid¹ when heated with hydrochloric acid.

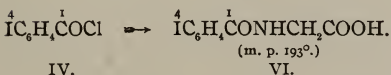
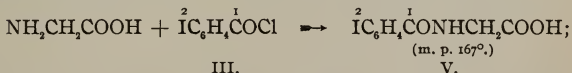
Our knowledge of iodine substituted hippuric acids is very limited. Only 2 iodhippuric acids are mentioned in "Beilstein's Handbuch."² One was prepared by J. Maier³ by warming hippuric acid with an alcoholic solution of iodine. While the structure of this acid is not known, it probably is to be represented by one of the two following formulas:



It is not identical with any one of the 3 iodhippuric acids that we describe in this paper.

The second iodhippuric acid mentioned was synthesized by Griess.⁴ It was prepared by treating diazohippuric acid with hydriodic acid, and is represented in the literature as a meta derivative. Griess does not state in his paper how he obtained his diazohippuric acid, but it is assumed that he synthesized it from metanitrohippuric acid, which was prepared by the nitration⁵ of hippuric acid.

We prepared ortho and paraiodhippuric acids by treating glycocoll, in alkaline solution, with orthoiodbenzoyl chloride,⁶ III., and paraiodbenzoyl chloride,⁷ IV., respectively.



The ortho acid melted at 167° and the para at 193°. Orthoiodhippuric acid possesses the peculiar property of depositing from hot water as an oil, which crystallized on standing.

¹ *Loc. cit.*

² Vol. II., 1187.

³ Z. f. Chem., 1865, p. 415. Am. J. Sci., [2], 39, 209.

⁴ Ber. d. chem. Ges., 1, 190 (1868).

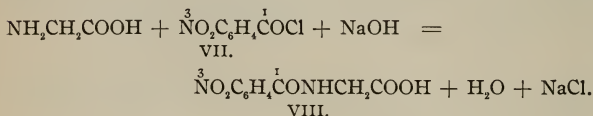
⁵ Schwanert: Ann. Chem. (Liebig), 112, 69. Conrad: J. prakt. Chem., [2], 15, 254.

⁶ Wachter: *Loc. cit.*

⁷ Hoffmann: Ann. Chem. (Liebig), 264, 167.

When the acid was impure we had much difficulty in getting it to assume a crystalline form. This behavior suggests why Mosse and Neuberg obtained their iodhippuric acid as a syrup.¹

Metaiodhippuric acid was obtained in the following manner: Metanitrohippuric acid, VIII., was prepared from glycoll and metanitrobenzoyl chloride, VII., according to the equation :



The nitro acid was then reduced to aminohippuric acid with ammonium sulphide.² When the amino acid was diazotized and warmed with potassium iodide, it was converted into metaiodhippuric acid. Griess gave no melting point for his acid. Our acid melted at 156°. It agreed in its crystalline form and solubility with the iodine acid described by Griess.

EXPERIMENTAL.



acid was obtained in the form of its sodium salt by treating an aqueous solution of 1.3 grams of aminoacetic acid and 1.4 grams of sodium hydroxide with 3.8 grams of orthiodbenzoyl chloride (Schotten-Baumann reaction). When the alkaline solution was acidified with hydrochloric acid the iodhippuric acid deposited as a colorless, crystalline solid. It was purified for analysis by recrystallization from hot water. It deposited, on cooling, as an oil, that finally crystallized in clusters of radiating needles. They melted at 167°, without effervescence, to a clear oil. Analysis (Kjeldahl) :

¹ "— resultiert eine Lösung der freien Säure, die sich beim Eindampfen als Syrup an den Gefäßwandungen abscheidet."

² Schwanert : Ann. Chem. (Liebig), 112, 70.

	Calculated for $C_9H_5O_3NI$.	I.	Found. II.
N	4.59	4.48	4.50

The orthoiodbenzoic acid and orthoiodbenzoyl chloride that were used in the above experiment were prepared according to the directions of Wachter.¹

o-Iodobenzoylaminoacetonitrile, $IC_6H_4CONHCH_2CN$.—A solution of aminoacetonitrile was prepared by dissolving 20 grams of the aminoacetonitrile sulphate² and 10 grams of sodium hydroxide in cold water. The calculated quantity of orthoiodbenzoyl chloride was then added to this solution, in small portions and the mixture thoroughly shaken. The nitrile separated as a colorless solid. The yield was practically quantitative. It deposited from alcohol in prisms, which melted, at 158° , to a clear oil. Analysis (Kjeldahl) :

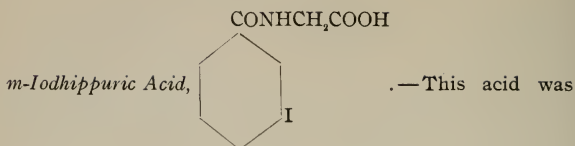
	Calculated for $C_9H_7ON_2I$.	Found.
N	9.80	10.00

Ethyl o-Iodhippurate, $IC_6H_4CONHCH_2COOC_2H_5$.—Dry hydrochloric acid gas was passed into a hot, alcoholic solution of the above nitrile for 3 hours. The solution was then evaporated to dryness. We obtained a crystalline residue that was washed with cold water to remove ammonium chloride. The ester was extremely soluble in alcohol and benzene. It was purified for analysis by crystallizing from a mixture of ligroin and benzene. It separated as an oil and finally crystallized in the form of irregular prisms, which showed signs of melting at 70° , and then melted, at 79° – 80° , to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_{11}H_{12}O_3NI$.	Found.
N	4.20	4.34

¹ Ber. d. chem. Ges., **26**, 1744.

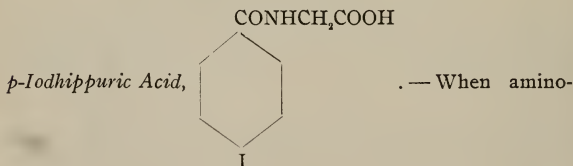
² Klages: *Ibid.*, **36**, 1511.



prepared by warming an aqueous solution of potassium iodide and metadiazohippuric acid.¹ It deposited from hot water in scales or thin plates that melted at 155°–156°. Analysis (Kjeldahl):

	Calculated for C ₉ H ₈ O ₃ NI.	Found.
N	4.59	4.9

The metaaminohippuric acid required for this preparation was obtained in the following manner: Metanitrobenzoic acid was first made according to the method described by Hübner,² and then converted into the chloride with phosphorus pentachloride.³ Metanitrohippuric acid was prepared by treating aminoacetic acid with metanitrobenzoyl chloride, according to Schotten-Baumann's reaction and the nitro acid was reduced to aminohippuric with ammonium sulphide.



acetic acid was treated with paraiodbenzoyl chloride, under the same conditions as used in the preparation of orthoiodhippuric acid, it was converted, quantitatively, into this acid. It was difficultly soluble in cold water, but deposited from hot water in plates that melted at 193°. Analysis (Kjeldahl):

	Calculated for C ₉ H ₈ O ₃ NI.	Found.
N	4.59	4.55

¹ Griess: Ber. d. chem. Ges., 1, 490.

² Ann. Chem. (Liebig), 222, 72.

³ Claisen and Thompson: Ber. d. chem. Ges., 12, 1943.

The paraiodbenzoic acid required for this experiment was prepared according to the method described by Körner,¹ by oxidizing paraiodtoluene with potassium bichromate and sulphuric acid.

p-Iodobenzoylaminoacetonitrile, $\overset{4}{\text{I}}\text{C}_6\text{H}_4\overset{\text{I}}{\text{C}}\text{ONHCH}_2\text{CN}$, obtained from paraiodbenzoyl chloride and aminoacetonitrile, in presence of excess of sodium hydroxide, was purified for analysis by recrystallization from alcohol. It deposited in prismatic crystals that melted at 191°–192°. Analysis (Kjeldahl) :

	Calculated for $\text{C}_9\text{H}_7\text{ON}_2\text{I}$.	Found.
N	9.80	9.55

Di-p-iodbenzoylaminoacetonitrile, $(\overset{4}{\text{I}}\text{C}_6\text{H}_4\overset{\text{I}}{\text{C}}\text{O})_2\text{NCH}_2\text{CN}$.—This was obtained as the chief product of the reaction in one experiment when we proceeded as follows : Three grams of aminoacetonitrile sulphate and 3 molecular proportions of sodium hydroxide were dissolved in water. When this solution was shaken with 5 grams of paraiodbenzoyl chloride the nitrile deposited as a white, crystalline solid. It crystallized from alcohol in clusters of radiating prisms that melted at 215°–216°. Analysis (Kjeldahl) :

	Calculated for $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{I}_2$.	Calculated for $\text{C}_9\text{H}_7\text{ON}_2\text{I}$.	I. Found.	II.
N	5.42	9.80	5.49	5.59

Ethyl p-iodhippurate, $\overset{4}{\text{I}}\text{C}_6\text{H}_4\overset{\text{I}}{\text{C}}\text{ONHCH}_2\text{COOC}_2\text{H}_5$, was prepared by saturating an alcoholic solution of the above nitrile with hydrochloric acid gas and then warming for a few hours on the steam-bath. It was purified for analysis by recrystallization from alcohol and deposited in plates that melted, at 128°–129°, to a clear oil. Analysis (Kjeldahl) :

	Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{NI}$.	Found.
N	4.20	4.44

p-Iodobenzoylanilide, $\overset{4}{\text{I}}\text{C}_6\text{H}_4\overset{\text{I}}{\text{C}}\text{ONHC}_6\text{H}_5$, prepared from aniline and paraiodbenzoyl chloride, was purified for analysis by recryst-

¹ Zeit. f. Chem., 1868, p. 327.

tallization from 95 per cent alcohol. It melted at 210° , without effervescence. Analysis (Kjeldahl) :

	Calculated for $C_{18}H_{10}ON_1$.	Found.
N	4.33	4.52

3,5-Dinitrobenzoylanilide, $(NO_2)_2C_6H_3CONHC_6H_5$, from 3,5-dinitrobenzoyl chloride¹ and aniline, crystallized from alcohol in needle-like prisms, that melted at 234° – 235° . Analysis (Kjeldahl) :

	Calculated for $C_{13}H_9O_5N_3$.	Found.
N	14.63	14.46

3,5-Dinitrobenzoylparatoluidide, $(NO_2)_2C_6H_3CONHC_6H_4CH_3$.—This compound was practically insoluble in water and the ordinary organic solvents. It did not melt below 280° . Analysis (Kjeldahl) :

	Calculated for $C_{14}H_{11}O_5N_3$.	I.	Found.	II.
N	13.95	13.8		14.1

3,5-Dinitrobenzoylorthotoluidide, $(NO_2)_2C_6H_3CONHC_6H_4CH_3$.—This was purified for analysis by crystallizing from alcohol. It melted at 241° – 242° . Analysis (Kjeldahl) :

	Calculated for $C_{14}H_{11}O_5N_3$.	Found.
N	13.95	14.2

BY WALTER C. CHALKER.

3,5-Dinitrobenzoylmethylanilide, $(NO_2)_2C_6H_3CON(CH_3)C_6H_5$.—This derivative deposited from alcohol in prismatic crystals that melted at 155° – 156° , without effervescence, to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_{14}H_{11}O_5N_3$.	Found.
N	13.95	14.1

3,5-Dinitrobenzoyldiphenylamine, $(NO_2)_2C_6H_3CON(C_6H_5)_2$.—This compound was soluble in warm alcohol. It deposited,

¹ Behrend and Heymann : J. prakt. Chem., [2], 69, 455.

on cooling, in prisms that melted, at 180° – 181° , to an oil. Analysis (Kjeldahl) :

	Calculated for $C_{19}H_{13}O_5N_3$.	Found.
N	11.57	11.8

3,5-Dinitrobenzoyl- α -naphthalide, $(NO_2)_2C_6H_3CONHC_{10}H_7$.—
This compound was extremely insoluble in water and the ordinary organic solvents. It melted, at 268° , to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_{17}H_{11}O_5N_3$.	Found.
N	12.46	12.50

NEW HAVEN, CONN.,
June 15, 1906.

SOME CONSTITUENTS OF THE POISON IVY PLANT.¹

BY S. F. ACREE AND W. A. SYME.

Rhus Toxicodendron.

Up to the present time only three important chemical investigations of the poison ivy plant have been recorded, namely, those of Khittel,² Maisch,³ and Pfaff.⁴ The object of their work was to obtain the poisonous principle of the plant, and their results may be briefly stated as follows: Khittel thought that the poison was a volatile alkaloid, but he did not prove by physiological evidence that he had obtained a toxic substance. Maisch obtained a volatile acid, which he called *toxycodendric acid*, by distilling an aqueous extract of the plant. His acid was similar to formic and acetic acids, but more like the latter. He produced physiological evidence, of a doubtful character, to show that it was poisonous. Pfaff showed that the volatile acid of Maisch was probably impure acetic acid, containing traces of the poisonous substance which he thought

¹ This paper is an abstract of a dissertation submitted to the Board of University Studies of the Johns Hopkins University by W. A. Syme, for the degree of Doctor of Philosophy. A more detailed account of the work will be found in the dissertation.

² Amer. J. Pharm., 1858, 542.

³ Proc. Amer. Pharm. Assn., 1865, 166. Amer. J. Pharm., 1866, 4.

⁴ J. Expt. Med., 2, 181 (1897).

was not volatile. He got from the plant a non-volatile oil, *toxicodendrol*, which he showed, by most reliable tests upon himself, to be the poison, or to contain it.

The present investigation was undertaken to see if more light could be thrown on the chemical nature of toxicodendrol. Soon after commencing work, however, it became apparent that the poison could be more intelligently studied if the substances associated with it in the plant were first identified. The scope of the work was, therefore, extended to an investigation of these other constituents.

The crude material for our work was prepared by Messrs. Parke, Davis and Company, of Detroit, Michigan, according to special instructions submitted to them: Fresh leaves and flowers of poison ivy were collected near Detroit and carefully inspected by a competent botanist. This material, which weighed 67.5 lbs., was completely macerated and put into 10 liter bottles, with ether. The mass was thoroughly shaken, water being added to make it more mobile. The ether was then separated and the extraction was repeated three times in the same way, to insure complete removal of the toxicodendrol. The ether extracts were combined, thoroughly dried with anhydrous sodium sulphate, and the ether was distilled off, the temperature being kept below 40° during the entire distillation. The residue, after the removal of the ether, was a thick, black, tar-like mass, weighing 3 lbs. 11 oz. In extracting the plant, about 24 gallons of ether were used. It is a significant fact, in regard to the volatility of the poison, that during the process of preparing this material, none of the employees engaged in the work were in any way affected, since proper precautions were taken and the utensils were handled with rubber gloves.

The crude ether extract, which will be designated as the "*original material*," was shipped to Baltimore in August and was kept in a cool place until November, when the investigation was begun. When the bottle was opened by the junior author there appeared to be an escape of vapor, and a nauseating odor suggesting crushed green leaves pervaded the atmosphere. Some days later irregular red patches appeared on his

face, though a mask of cotton cloth was worn during the work, and his hands were protected by rubber gloves.

The first experiment was to try to distil out the toxicodendrol from the original material with the aid of a vacuum pump. At a temperature of 140° – 150° (2 mm.), the material carbonized and nothing passed over.

It was then thought that perhaps the oil could be converted into an ester which might be more volatile and could be distilled. Twenty grams of the original material were dissolved in 100 cc. of absolute alcohol, containing 3 grams of hydrochloric acid gas, and the mixture was heated 10 hours on a water-bath, under a return condenser. After the heating, the mixture had a delightful ethereal odor. The flask was closed and left standing several weeks, while other work was in progress. The ester solution was then put in a vacuum desiccator, over sulphuric acid, and the alcohol evaporated. A black, tarry, solid mass was left having the ester odor. It was extracted with warm water and filtered from insoluble tar. The filtrate was green and had the ethereal odor. It was shaken out with ether; the ether layer was blood-red and the aqueous portion deep green. The extraction with ether was continued until the water layer was no longer green. The combined ether extracts were evaporated in a desiccator, without heat. A black, tar-like solid was left, very much like the original material, but it had the ester odor. It was partly soluble in water and readily dissolved in alcohol. The alcoholic solution was tested on the skin and found not to be poisonous. The ester, or mixture of esters, was not investigated further in this connection, but was later shown to give the reactions for gallic acid and methyl furfuraldehyde. These reactions will be referred to in connection with other experiments.

Further preliminary work showed that the original mixture was very complex and that it would be necessary to fractionate it and examine the fractions separately. Chlorophyll could not be removed because the solvents for chlorophyll, *viz.*, alcohol, ether, carbon bisulphide, etc., dissolve large quantities of the mixture.

Some of the original material was extracted with 50 per cent

alcohol, filtered from insoluble tar, and the following experiments were performed with the filtrate *F*.

(1) A portion was distilled under diminished pressure and a yellow, acid liquid was obtained. This was shaken with ether and the latter evaporated. A small quantity of a yellow solid was left. The substance was not volatile enough to justify the use of this method for getting it.

(2) A precipitate obtained by adding lead acetate, in 50 per cent alcohol, to a portion of the filtrate *F*, was suspended in water, decomposed by hydrogen sulphide, shaken with ether, and the ether evaporated. The residue, after drying in a desiccator, was a yellow solid, apparently the same as that obtained by distillation in (1) above.

(3) Another portion of the alcoholic filtrate *F* was filtered through bone-black. The colorless filtrate was, apparently, pure alcohol and water, everything in solution having been removed by the bone-black.

In precipitating an alcoholic solution of the crude material with a solution of lead acetate, it was noticed that at least two kinds of precipitates were formed. The part deposited first was darker in color than that thrown down later. Pfaff used the last fractions in obtaining his oil, and stated that these precipitates consisted of the lead compound of the oil in a pure state. The authors found, by experiment, that the darker part was soluble in ether while the lighter portion was not. This indicated that the former consisted of tarry matter which was brought down mechanically, or which separated out when the alcoholic solution was diluted by the lead acetate solution, or that possibly it was a lead compound soluble in ether. To test this point an experiment was made as follows: Some of the crude material was thoroughly extracted with 50 per cent alcohol. The insoluble tar was then treated with 95 per cent alcohol, when most of it dissolved; the solution was filtered and lead acetate, in 50 per cent alcohol, was added. A greenish-colored precipitate was formed which was filtered off and found to be completely soluble in ether and soluble, to a considerable extent, in strong alcohol. These experiments suggested that the light-colored lead compound, which was thought to con-

tain the poison, could be purified by extraction with ether in a Soxhlet apparatus more conveniently than by the tedious process of fractional precipitation. Further preliminary experiments showed that 50 per cent alcohol extracted from the original material all of the substance or substances which gave the light-colored precipitate and dissolved only a small amount of the tar.

Some of the original material (288 grams) was then extracted several times with 50 per cent alcohol and filtered; the insoluble tar was washed and saved for examination. To the filtrate was added an excess of a solution of lead acetate, in 50 per cent alcohol. The large precipitate, which will be designated as "*Precipitate A*," was filtered and drained by suction in a Büchner funnel. The alcoholic "*Filtrate A*" was saved. *Precipitate A* was extracted with ether in Soxhlet extractors until the ether came over practically colorless, the operation being interrupted from time to time to stir up the precipitate in the thimble. The green-colored ether solution was saved for future examination. The lead precipitate, after being extracted with ether and dried, weighed about 116 grams. A portion of this lead compound was decomposed by hydrogen sulphide in a mixture of water and ether, which was well shaken during the operation. The ether was separated, filtered and evaporated under diminished pressure, without heat, there remained a yellow, oily residue having a pleasant odor. When the ether and water were completely removed in a vacuum desiccator, a hard, brittle, yellow resin, weighing about 16 grams, was obtained. It was soluble in alcohol, had a strong acid reaction and was free from nitrogen¹ and sulphur. The tests for nitrogen were made by the Lassaing and soda lime methods; this element was found very readily by means of soda lime in the tar left after extracting the original material with 50 per cent alcohol, but was not found by the Lassaing test. Sulphur was detected by means of sodium nitroprusside, after fusing the residue with sodium. The main portion of the lead compound was decomposed under alcohol, by hydrogen sulphide, filtered and the alcoholic filtrate evapo-

¹ Amer. J. Pharm., 77, 255 (1905).

rated *in vacuo*. The same yellow, acid resin was obtained. Experiments continuing through several weeks were made in applying solutions of this resin to rats, rabbits and guinea pigs. Finding it to be without effect upon these animals it was tried on the junior author and found not to be poisonous. Whenever it is stated in this paper that a solution was poisonous or not poisonous, the test was made by the junior author upon himself.

Gallic Acid.

An alcoholic solution of the resin was just neutralized with potassium hydroxide. During the titration the solution rapidly became dark brown. After neutralization it was shaken with ether; the water solution remained brown while the ether layer was nearly colorless and contained practically no dissolved substance. A portion of the water solution of the potassium salt, on being acidified with sulphuric acid and allowed to stand over night, deposited a slight precipitate with lead acetate, somewhat similar to the original lead precipitate A, and also slight precipitates with salts of zinc, mercury, copper and silver (with reduction). It gave a bluish-black color with impure ferrous sulphate and a dark color with ferric chloride. It reduced ammoniacal silver nitrate and Fehling's solution. These experiments indicated the presence of a tannin compound. An alcoholic solution of the resin gave the same color reactions with iron salts as did the potassium salt.

Further tests with a solution of the resin in dilute alcohol, and with an aqueous solution of the acid precipitated by adding sulphuric acid to a solution of the resin in potassium hydroxide, led to the conclusion that the acid is gallic acid. These tests were the following :

(1) Boiling with an excess of potassium hydroxide gave a black substance, tauromelanic acid.

(2) The acid was not precipitated by gelatin.

(3) On the addition of potassium cyanide a transitory, red color was produced, which reappeared on shaking with air.

Gallic acid is distinguished from tannic acid by tests 2 and 3.

At later stages in the work the potassium, barium and

sodium salts of gallic acid were obtained and, finally, the pure acid was made by decomposing the sodium salt with sulphuric acid and crystallizing from water. The melting point of the acid corresponds with that of gallic acid; it melted, with decomposition, at about 230° .

For further identification, some of the acid was converted into the ethyl ester by the method of Grimaux.¹ The ester obtained agreed in melting point and other properties with that described by Grimaux. The same compound was also made from gallic acid from another source and the esters agreed in properties. A mixture of the two specimens melted within the limits given for the ethyl ester of gallic acid, 156° – 159° .

While the tests leading to the identification of gallic acid were being made, another series of experiments was in progress. Eleven and one-half grams of the resin obtained from lead precipitate *A*, by decomposition with hydrogen sulphide, were treated with 0.1 N potassium hydroxide, added from a burette until the acid was exactly neutralized. All went into solution. On shaking with ether, some of the potassium salt separated out and was saved for examination. The solution became dark brown on exposure to the air and got darker as the work proceeded. The acid in solution as a potassium salt was precipitated out in 4 fractions, by adding one-fourth the amount of 0.1 N sulphuric acid required to neutralize the potassium hydroxide used.

The precipitates were filtered off and examined. The first was small in amount, gummy and difficult to filter. The solution was shaken with ether after each precipitate had been filtered off. The succeeding precipitates were in better condition, but were not pure. All appeared to be impure gallic acid, which had become brown by absorption of oxygen, but they were saved to be tested for poison. After the last fraction had separated the filtrate was shaken several times with ether and retained for further examination, which will be described under "rhamnose." This filtrate is designated as *B*.

A portion of the resin obtained from lead precipitate *A* was tested and found not to be poisonous, as already mentioned.

¹ Bull. Soc. Chim., [2], 2, 95 (1864).

By this test, all the substances contained in the lead precipitate A, after its extraction with ether in the Soxhlet apparatus, were eliminated from the possible poisonous substances. The poison must, therefore, have been extracted by the ether.

A portion of the original poisonous material was treated with 50 per cent alcohol and filtered from insoluble tar. The filtrate was precipitated in 6 fractions by lead acetate. The last fractions were lighter in color and, apparently, much purer than the first. The sixth lead precipitate was decomposed by hydrogen sulphide. The light yellow, aqueous solution was tested and found not to be poisonous. It gave the characteristic reactions for gallic acid. The poison, if precipitated at all by lead acetate, must have been contained in one of the preceding fractions. Later experiments showed that it is brought down, partly mechanically and partly as a lead compound, in the first precipitation.

Fisetin.

Some of the original material was extracted with hot water to remove gallic acid and filtered from tar while hot. The filtrate had a deep yellow color. On cooling over night, an olive green precipitate separated out which, when dry, was a light powder. It was practically insoluble in cold water, but soluble with great difficulty in boiling water, from which it separated in yellow flakes; it dissolved slightly in ether and acetic acid and readily in alcohol. The solutions, which were not acid to litmus, gave a dark color with ferric chloride, an orange red precipitate with lead acetate, which was easily soluble in acetic acid, and an orange yellow precipitate with stannous chloride. These properties and reactions indicated that the substance was the dye-stuff fisetin and that it occurs in the free state in this plant, though it is usually found as a glucoside of fisetin combined with tannic acid.

The substance which separated from the boiling water solution was further purified by dissolving it in a small quantity of hot alcohol and adding hot water. On cooling, the yellow compound separated out in a flocculent condition. Examined under a microscope, the flakes appeared to be made up of

masses of fine crystals. The substance was found to have the characteristic properties of fisetin described by Schmid,¹ and on fusion with potassium hydroxide² gave protocathechuic acid and phloroglucinol. These substances were identified by characteristic tests.

Rhamnose.

Schmid³ obtained a sugar solution by the decomposition of a fisetin glucoside from *Rhus cotinus*, and Perkin⁴ obtained the same from a glucoside in *Rhus rhodanthema*. They thought that the sugar in both cases was isodulcite, but they did not isolate it. Assuming that the free fisetin found in *Rhus toxicodendron* had its origin in the decomposition of a fisetin glucoside by natural processes, it was reasonable to suppose that the sugar would also be found in the free state, although, with one or two possible exceptions,⁵ rhamnose has not been found except as a glucoside body.

Since rhamnose forms a lead compound, the sugar, if present, should be found in the first lead precipitate, A, and also in the filtrate A in case it is not completely precipitated in the presence of acetic acid and alcohol.

About 2 liters of the filtrate A were examined first. It had a light yellow color, contained an excess of lead acetate and was acid from the acetic acid liberated in the precipitation of the lead compound A. This filtrate was evaporated to dryness, under diminished pressure, to remove alcohol, water and acetic acid. The clear distillate had a peculiar odor suggesting both tea and amyl formate. It was saved for examination and was found to be not poisonous. The residue in the dish, after evaporation, was a tough, reddish brown, gummy mass which could be drawn out into fine threads. It had a pleasant, sweet odor. It was extracted several times with hot water, each portion being filtered. A yellow brown powder remained undissolved and was saved. The combined filtrates deposited more of the yellow solid on standing. The filtered liquid was

¹ Ber. d. chem. Ges., 19, 1740.

² *Ibid.*, 19, 1747; Ann. Chem. (Liebig), 112, 97.

³ *Loc. cit.*, 19, 1738.

⁴ J. Chem. Soc., 71, 1194.

⁵ Chem. Ztg., 23, Rep., 177.

freed from lead by hydrogen sulphide. The solution then had a lemon yellow color, a sweet odor and was acid from acetic acid. On concentrating the solution by evaporation and making a small portion of it alkaline with sodium hydroxide, the yellow color came out very intensely by warming with alkalis or barium hydroxide.¹ Rhamnose is colored yellow under these conditions. The alkaline solution reduced Fehling's solution and ammoniacal silver nitrate, indicating the presence of a sugar. Another portion of the solution gave a slight precipitate with phenylhydrazine, in the cold. The remainder of the solution was evaporated to dryness, extracted with water, filtered and again evaporated. A dark, sticky syrup was left which was only partly soluble in water. This was treated with water, filtered and the filtrate evaporated, the water being replaced from time to time to remove acetic acid. Finally, the liquid gave the following tests for rhamnose, besides those already mentioned :

- (1) With α -naphthol² and sulphuric acid, a purple violet color.
- (2) With thymol² and sulphuric acid, a red color.
- (3) With resorcinol³ and sulphuric acid, a red color.
- (4) With orcinol⁴ and hydrochloric acid, a red color.
- (5) With ammonium picrate and sodium picrate, a yellowish red color.
- (6) With phloroglucinol and hydrochloric acid, a red color.
- (7) It decolorized an alkaline solution of potassium ferricyanide.
- (8) It gave a white precipitate with lead acetate.

The filtrate *B* (p. 307), from which gallic acid was precipitated by sulphuric acid in 4 fractions, was saved to be examined for sugar. To remove gallic acid completely, and other vegetable matter, it was shaken out several times with ether and was kept at a low temperature with salt and ice for a long time. It was left standing for several weeks, during the course of which more brown matter separated and was filtered off.

¹ Chem. der Zuck., I, 177.

² *Ibid.*, I, 188.

³ Rayman: Bull. Soc. Chim., 47, 668 (1887).

⁴ Acides Gummiques, Garros.

The filtrate was evaporated to a small bulk, cooled and filtered from crystals of potassium sulphate. The filtrate was evaporated to dryness, the residue taken up in water and filtered through bone-black. Addition of alcohol caused complete precipitation of potassium sulphate. The solution then gave the above-mentioned, characteristic tests for rhamnose.

All attempts to get the osazone of the sugar by Fisher's method failed, probably on account of the small quantity of sugar present. The plant, it will be remembered, was originally extracted with ether, in which rhamnose is practically insoluble. The tests above described, however, can leave no doubt as to the identity of the sugar.

Additional evidence that the sugar is rhamnose was obtained by a method for testing for the presence of this sugar described by Maquenne.¹ This consists in converting the sugar into methyl furfuraldehyde, by distilling the substance to be tested with dilute sulphuric acid. The presence of methyl furfuraldehyde in the distillate is shown by a green color with alcohol and sulphuric acid. "This procedure is applicable to extracts as well as to entire plants, and has the advantage that it does not require the separation of isodulcite, the crystallization of which is often very slow, and at times impossible, when it is mixed with other very soluble substances."²

The experiment was tried with the crude ether extract of the plant, according to the directions of Maquenne, and the green color with alcohol and sulphuric acid was obtained from the thicker, oily portion of the distillate. This test can be made with hydrochloric acid³ as well as with sulphuric. Therefore, the color test was tried with the ester mixture prepared in one of the early experiments by boiling the original plant material with hydrochloric acid and alcohol. Methyl furfuraldehyde was found here also, indeed better results were obtained than by following Maquenne.

The presence of free rhamnose has thus been shown in the original material, in the first precipitate by lead acetate and in the filtrate from this precipitate. Experiments to be described

¹ Ann. Chim. Phys. [6], **22**, 93 (1891).

² *Loc. cit.*

³ Biochem. der Pflanz., I., 210.

under "*The Poison*" showed that the ether extract from the Soxhlet apparatus contained a substance which yielded rhamnose when hydrolyzed by dilute sulphuric acid.

The presence of free gallic acid, fisetin and rhamnose in the plant can be readily explained by a series of assumptions for which there is a considerable amount of experimental evidence. There is reason to believe that tannin-like bodies are formed at the expense of chlorophyll,¹ that complex tannin compounds can be broken down by acetic acid, which is also found in *Rhus toxicodendron*, into a tannic acid and a glucoside; for example, "fustin-tannide"² yields tannic acid and fisetin glucoside; and, finally, that the glucoside can be hydrolyzed by acids or enzymes giving, in the sumach plants, fisetin and rhamnose.

Nitrogenous ferments which can effect the hydrolysis of glucosides and give rise to sugars are frequently found in plants, for example, emulsin in almonds, myrosin in mustard, and erythrozym in madder. Acree and Hinkins³ found that diastase, pancreatin and a number of other enzymes cause the hydrolysis of triacetyl glucose with the formation of glucose and acetic acid. Stevens⁴ obtained a nitrogenous oxidizing enzyme from *Rhus vernicifera*. The close relationship between the poisonous species of *Rhus* would lead us to suppose that the same soluble ferment exists in poison ivy, though it was not detected in the original material used in these experiments, probably because the plant was extracted with ether in which the enzyme is insoluble. The existence of such a soluble ferment would explain the presence of free sugar and free fisetin.

The Poison.

Some of the original poisonous material (288 grams) was extracted with 50 per cent alcohol, and this alcoholic solution was precipitated with lead acetate in the manner already described (p. 304). The lead precipitate so obtained was extracted with ether in Soxhlet extractors and, after the extraction, was found by test to be free from poison. Therefore, the poison, if precipitated by the lead acetate, must have been ex-

¹ Compt. rend., 115, 892.

² Schmid: Ber. d. chem. Ges., 19, 1736.

³ THIS JOURNAL, 28, 370.

⁴ Amer. J. Pharm., 77, 255 (1905); 78, 53 (1906).

tracted by the ether. This ether solution had a dark green color, and was acid from acetic acid brought down in the lead precipitate. The ether was evaporated in a vacuum desiccator without heat and there remained a small quantity of an acid mixture of water and a soft tar; the watery part was colored green, showing that the tar was soluble to some extent in dilute acetic acid. The mixture had the peculiar odor of the original material. A small drop of the green, watery part was applied to the wrist, allowed to remain a few minutes and was then removed by absorbent paper, but the spot was not washed. Itching and reddening of the skin commenced within 24 hours. At the end of 48 hours there was a well-developed case of poisoning. This was cured by immersing the arm in a hot solution of potassium permanganate.

A small portion of the poisonous mixture was dissolved in alcohol, and this solution was divided into 3 parts. The first part was treated with ferric chloride, but it gave no color reaction. Another portion of the alcoholic solution was diluted with water; it became turbid. The third portion gave a dirty green precipitate with lead acetate, which seemed to come down more readily when the solution was diluted with water. The main portion of the poisonous mixture was then dissolved in 95 per cent alcohol and lead acetate, in 50 per cent alcohol, was added. The precipitate was filtered, washed and decomposed by hydrogen sulphide, in a mixture of water and ether. The ether solution was filtered and evaporated. The residue was a tar which, on standing in a desiccator for some time, became dry enough to be broken into sticky lumps. An alcoholic solution of this substance gave a dark color with ferric chloride and a light colored precipitate with lead acetate.

To get more of the poisonous tar for study, 233 grams of original material were extracted with 95 per cent alcohol. Strong alcohol was used in order to dissolve as much of the tar as possible. The solution had a dark, greenish color but was somewhat yellow in thin layers. The undissolved tar was filtered off and extracted twice again in the same way. The tar left after the third extraction was only slightly soluble in alcohol, and its solution was not poisonous. The 3 filtrates

from these 3 extractions were precipitated separately by lead acetate, in 50 per cent alcohol. The first precipitate was largest, darkest in color and carried down the most tarry matter. The second was light green. The third, which was quite small, was black and was not a lead compound at all, but some of the tar which separated out on diluting the strong alcohol with the weaker containing lead acetate. It was soluble in ether and less soluble in alcohol. The alcoholic solution of this third portion gave no precipitate with hydrogen sulphide. The first and second lead precipitates were filtered by suction and washed with water. They were kept a day or two in a desiccator over sulphuric acid, but did not become completely dry. The weight of these two moist precipitates together was 172 grams. They were combined and extracted with ether in Soxhlet extractors, which were kept in operation during work hours for 3 days.

In the meantime the alcoholic filtrates from these lead precipitates were combined and concentrated on the water-bath, by distilling off 2 liters of alcohol. The alcohol obtained had the peculiar odor of the original material, but was not poisonous.

After a long extraction of the lead precipitate in the Soxhlet extractors, the green, ether solutions were combined and washed by shaking them with water, to remove lead acetate and acetic acid, in case any should have been held in the lead precipitate. The ether was distilled off at a low temperature and there remained a soft tar, a portion of which was not completely soluble in 95 per cent alcohol. The alcoholic solution had a greenish-yellow color and was poisonous. The tar was also partly soluble in acetic acid, and this solution was found to contain lead. Thinking that the lead acetate had not been completely washed out, the main part of the tar was dissolved in ether and shaken with water. The wash water continued to give a test for lead as long as the washing was continued. This indicated the probable hydrolysis of an unstable lead compound. To remove the lead, hydrogen sulphide was passed into the ether solution mixed with water. Lead sulphide was filtered off and the ether was evaporated. A small

portion of the tar residue, in alcoholic solution, gave a color reaction with ferric chloride. As this may have been due to traces of lead gallate dissolved in the extraction with ether and afterwards decomposed by hydrogen sulphide, the main portion of the tar was redissolved in ether and shaken with water until it no longer reacted with ferric chloride. The ether was then evaporated and a soft, black, poisonous tar or gum of uniform consistency was left, which was proved to be free from gallic acid and lead. These experiments showed that some of the poison was precipitated as a lead compound soluble in ether and some was brought down mechanically in the free state. To see if the extraction with ether in the Soxhlet apparatus was complete, the residue in the thimbles was decomposed by hydrogen sulphide and shaken with ether. The dark-colored, ether solution was freed from gallic acid by shaking with water and dilute sodium carbonate solution, and was evaporated. A small quantity of tar was obtained which was added to the main portion.

A solution of the poisonous tar in 95 per cent alcohol did not reduce Fehling's solution and did not give a precipitate with lead acetate, except for the separation of a small quantity of tar, which was not a lead compound. The lead compound of the poison was, apparently, soluble in 95 per cent alcohol as well as in ether, for it would not precipitate in this medium, although it was found in the original precipitate by lead acetate. The alcoholic solution of the tar became turbid on diluting with water.

A portion of the tar was distilled, under diminished pressure, with acetic acid, which is present in the plant. It was soluble to some extent in the acid. The temperature did not go higher than 55° during the distillation. A tube containing cotton, moistened with sweet oil, was placed between the receiver and the water suction, so that the uncondensed vapors would have to pass through the cotton. This cotton was rubbed on the skin and was not poisonous. The yellow distillate collected in the receiver was also tested and was not poisonous. This proves that the poison, after its removal from the plant, is not volatile with the vapor of acetic acid.

Hydrolysis of the Poison.

About 5 grams of the tar, free from gallic acid and sugar, were dissolved in alcohol and dilute, 2 per cent, sulphuric acid was added, which caused a separation of some of the tar. The mixture was heated on a water-bath during work hours, for 4 days. A purple and green fluorescent solution was formed, though much tar was left apparently unchanged. The alcohol was evaporated off and the solution filtered from tar. The fluorescent filtrate was shaken with ether, by which the green substance was removed, leaving the solution purple. The ether left, on evaporation, a small quantity of a green material having a pleasant, ester odor. It was not further examined. A portion of the purple solution was exactly neutralized with sodium carbonate. This liquid gave a blue-black color with ferric chloride, which became red on the addition of another drop of sodium carbonate, indicating the presence of gallic acid. It also reduced Fehling's solution.

Another portion of the purple solution was made alkaline with sodium carbonate. A reddish-brown, flocculent precipitate was formed and was filtered off. The filtrate did not give any color with ferric chloride, but it reduced Fehling's solution. It also gave the test for rhamnose with α -naphthol.

The main portion of the purple solution was made alkaline with sodium carbonate; the precipitate was filtered off and dissolved in acetic acid. The solution was yellow and gave a reaction with ferric chloride similar to that of gallic acid. The filtrate from the precipitate obtained with sodium carbonate was concentrated by evaporation until sodium sulphate began to crystallize out. Alcohol was added to precipitate this salt completely; the mixture was heated and filtered. The alcoholic filtrate was concentrated to a syrup which reduced Fehling's solution and gave the characteristic test for rhamnose already mentioned. By this hydrolysis, the tar was split up into rhamnose and some form of gallic acid which could be precipitated by sodium carbonate. The compound, whose acetic acid solution was yellow, probably also contained fisetin. This statement is based on the results of the experiment described in the next section.

Decomposition of the Poison with Acetic Acid.

A portion of the poisonous tar was heated in an open dish with strong acetic acid. The tar seemed to be decomposed to some extent, giving a yellow substance. Acetic acid was added from time to time as it evaporated. After several evaporations, water was added, the mixture was heated to boiling and filtered. This filtrate, "No. 1," will be mentioned later. The residue in the dish consisted of undecomposed tar and an olive green, flaky substance, which latter was heated with a fresh portion of glacial acetic acid. Water was added and the mixture was boiled and filtered. The filtrate had a deep yellow color, suggesting fisetin. It was shaken out with ethyl acetate, which became colored yellow. A portion of the ethyl acetate solution gave an orange red precipitate with lead acetate, showing the presence of fisetin. The ethyl acetate was removed from the remainder of the solution by evaporation and the yellow residue was taken up in alcohol. This alcoholic solution gave the characteristic reactions for fisetin with stannous chloride, potassium hydroxide, ferric chloride and Fehling's solution.

Filtrate No. 1, obtained by heating the poisonous tar with acetic acid and hot water, as described above, was investigated as follows: A portion of it gave a reddish-colored precipitate with sodium carbonate, as in the case when the tar was hydrolyzed with sulphuric acid. The remainder was nearly neutralized with sodium carbonate and lead acetate was added, in excess, to remove gallic acid. The excess of lead was precipitated with sulphuric acid, and the sulphuric acid removed by barium carbonate. The solution, on evaporation, reduced Fehling's solution to some extent, but a white precipitate was also formed.

In this experiment, gallic acid and fisetin, and probably sugar, were formed by the decomposition of the poisonous gum with acetic acid, the acid found in the plant by Pfaff. The presence of free gallic acid, fisetin and rhamnose in the plant can be explained by the natural hydrolysis of a complex gum or tar, or of a constituent thereof.

The poisonous property is lost in the general rearrangement which takes place during hydrolysis, but the poisonous tar was not hydrolyzed by boiling with a dilute solution of sodium carbonate.

It was found, as has been stated elsewhere, that the lead compound of the poison could not be precipitated in 95 per cent alcohol. Further experiments, however, showed that on extracting the poisonous gum with 50 per cent alcohol, a portion of it dissolved, and this solution gave a precipitate with lead acetate, which was a true lead compound. The remainder of the purified tar, about 10 grams, was treated with 50 per cent alcohol and filtered. Very little dissolved in alcohol of this strength, but on the addition to the solution of lead acetate, in 50 per cent alcohol, a light colored precipitate was formed, which became dark on standing. It was filtered off, washed free from lead acetate, decomposed by hydrogen sulphide and shaken out with ether. The ether left, on evaporation, a yellow, resinous substance having a faint odor like garlic. By drying in a desiccator, a small quantity of solid, yellow resin was obtained which was completely soluble in alcohol. A very small drop of this solution applied to the skin on the end of a glass rod, which had been drawn out to a point, caused an eruption in about 36 hours. Following the nomenclature used by Maisch and Pfaff, this substance will be designated as *Toxicodendrin*.

The filtrate from the lead precipitate just described was freed from the excess of lead acetate by means of hydrogen sulphide, and was found to be poisonous, showing that the precipitation by lead acetate was not complete even in 50 per cent alcohol. On spontaneous evaporation of the solution a yellow, sweet smelling resin was left.

A portion of the alcoholic solution of the toxicodendrin gave a dark coloration with ferric chloride, but did not reduce Fehling's solution and was slightly acid to litmus.

To see whether the toxicodendrin could be hydrolyzed, the remainder was dissolved in alcohol and dilute sulphuric acid was added. A fine, white precipitate was formed at once which, on standing, rose to the surface as a light, flocculent

substance. The mixture was heated for several days on a water-bath, filtered from unhydrolyzed resin and the filtrate neutralized and concentrated in the way already described. The solution obtained reduced Fehling's solution. Not enough was available for further sugar tests, but all the hydrolysis experiments point to the conclusion that the poisonous substance is a rhamnoside, and is the source of the sugar in the plant.

The reaction with ferric chloride, observed whenever a lead compound of the poison is decomposed by hydrogen sulphide, may be explained by the formation of traces of gallic acid or fisetin through the action of the weak acids present.

The supply of purified poisonous tar having been exhausted in the preceding experiments, further study of the active principle is postponed until more can be prepared. It is highly desirable to investigate the white precipitate formed by the addition of sulphuric acid to an alcoholic solution of the toxicodendrin.

Oxidation of the Poison with Nitric Acid.

When the purified poisonous material (p. 312) was extracted with 50 per cent alcohol only a small quantity was dissolved, as was stated above. The insoluble residue was treated with fuming nitric acid. A violent reaction took place at once, with a copious evolution of red fumes and heat. When the reaction was over, a sticky, red, gummy mass was left which was slightly soluble in cold water and readily soluble in warm alcohol. The water extract was yellow and the alcoholic solution red. That the water extract contained picric acid was shown by the following experiments:

(1) A portion was gently warmed with a few drops of a strong solution of potassium cyanide and 2 drops of sodium hydroxide. The red color of potassium isopurpurate was formed.

(2) A portion of the water solution was heated with glucose and a few drops of sodium hydroxide. The deep red color of picraminic acid was produced.

(3) A few drops of an ammoniacal solution of copper sul-

phate was added to the water extract. A yellow-green precipitate was formed.

(4) The water extract dyed silk, but did not dye cotton cloth.

Distillation of the Tar with Soda Lime.

About 25 grams of the tar, left after extracting the original material with hot water, was dissolved in ether and poured into a glass retort containing soda-lime. The ether was distilled, leaving the tar intimately mixed with the soda-lime. The retort was then gradually heated. Vapors and liquid were given off, both of which turned red litmus blue and had a strong odor like tobacco smoke. No odor of ammonia was detected.¹ At the high temperature of the triple burner, a semisolid, red, greasy substance collected in the condenser tube and closed it. This material had the same powerful odor as the liquid portion of the distillate. The clear, watery portion of the distillate was separated from the thicker parts, and was proved, by the following characteristic tests, to contain pyrrol and pyridine derivatives:

(1) Wood moistened by hydrochloric acid was turned red by it.

(2) Colorless fumes were formed when brought near hydrochloric acid. When mixed with hydrochloric acid, a red insoluble substance was formed.

(3) It precipitated the hydroxides of iron, gave a light blue precipitate with copper sulphate and a white precipitate with mercuric chloride.

The greasy, semisolid mass was extracted with 10 per cent hydrochloric acid and filtered. On the addition of a solution of mercuric chloride to the red filtrate a brown, flocculent precipitate was formed. It was filtered off and distilled with sodium hydroxide, but the distillate did not contain pyridine.

Summary.

Leaves and flowers of the poison ivy plant were extracted with ether and the ether was removed by evaporation. In the

¹ *Vide*, Amer. J. Pharm., 77, 256.

residue, the following substances were found and studied. Gallic acid, fisetin, rhamnose and a poisonous tar, gum or wax.

The lead compound of the poison was soluble in ether; which gives a means of separating the poisonous from the non-poisonous matter in one operation.

The poison was not volatile with the vapors of acetic acid or alcohol.

The poisonous tar or wax was decomposed by acids and yielded gallic acid, fisetin and rhamnose, showing the probable source of these compounds in the plants, and indicating that the poison is a complex substance of a glucoside nature.

It was found that a portion of the poisonous material could be precipitated by lead acetate from a solution of the purified tar in 50 per cent alcohol.

All cases of poisoning developed on the junior author were easily cured with potassium permanganate.

The following method is suggested for obtaining the poisonous substance from the plant. Extract the plant with alcohol, filter and precipitate at once with lead acetate. Wash the precipitate, dry and extract it with ether in loosely filled Soxhlet extractors. Combine the ether extracts, mix with water and pass in hydrogen sulphide. Separate the water and the ether solution, and filter the latter. Wash the ether solution thoroughly by shaking with water, and then evaporate at a low temperature.

JOHNS HOPKINS UNIVERSITY,
June 1, 1906.

OBITUARY.

RUDOLF KNIETSCH.

Dr. Rudolf Knietsch died at Ludwigshafen on May 28, 1906. The whole of his active career was passed in the service of the "Badische Anilin-und Soda-Fabrik," which he entered exactly 22 years before the date of his death. During this period Knietsch had won for himself one of the foremost places in the ranks of technological chemists. We owe it to him that liquid chlorine became an article of commerce. His researches, carried on during 10 years, resulted in the applica-

tion of the "contact process" to the manufacture of concentrated and dilute sulphuric acid, and he took an active share in the technical synthesis of indigo. In 1904 the Verein deutscher Chemiker conferred on Knietzsch the "Liebig" gold medal.

REVIEWS.

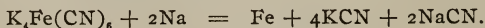
THE CYANIDE INDUSTRY PRACTICALLY AND THEORETICALLY CONSIDERED. By R. ROBINE and M. LENGLIN, translated by J. ARTHUR LECLERC, PH.D., with an appendix by C. E. MUNROE, PH.D. First edition. London: Chapman & Hall; New York: John Wiley & Sons. 1906. pp. 408. Price, \$4.00.

The authors offer, in this book, a complete description of the chemistry of cyanogen and its derivatives from chemical and industrial points of view. In Part I. a description of the individual cyanogen derivatives is followed by a study of their analytical properties, of methods of analysis, of toxicological methods and of thermochemical data; these last are quoted from Berthelot.

The processes for manufacturing cyanides are classified as non-synthetic and synthetic; the first class includes 10 patented processes for extracting cyanides from sulphocyanides. The authors describe 28 synthetic processes, utilizing atmospheric nitrogen, 24 utilizing ammonia and several special processes besides. The manufacture of ferrocyanides, ferricyanides, sulphocyanides and Prussian blue are described with equal fulness. An appendix by Dr. Munroe, containing a study of the use of cyanides for the extraction of precious metals from their ores and a descriptive list of the U. S. patents on the subject, closes the book.

While the authors describe historically so many patented processes, they discriminate clearly between those which have present or prospective value and those which are technically valueless; their criticisms on the different processes are very interesting and show a thorough knowledge of the subject.

The following are some of the more important and successful cyanide processes. Rossler and Harlacher's, which depends on this reaction, fused

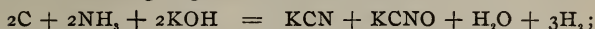


Playfair's, by fusing sulphocyanide with zinc,



Frank and Caro's process and those of Dziuks and of the General Electric Chemical Co., all depending on the action of

atmospheric nitrogen on carbides. That of the Stassfurter Chemische Fabrik, depending on the interaction of ammonia, heated charcoal and alkali, and said, by the inventors, to occur in the following stages: At dull red heat,



on increasing the heat the cyanate is reduced to cyanide by the carbon. Castner's famous method, utilizing ammonia and sodium; in the first stage of this process sodamide is made, $\text{NH}_3 + \text{Na} = \text{NH}_2\text{Na} + \text{H}$; the fused sodamide is then treated with heated charcoal, forming cyanide— $\text{NH}_2\text{Na} + \text{C} = \text{NaCN} + \text{H}_2$. The process of the Deutsche Gold und Silber Scheide Anstalt, which combines the advantages of the processes of Frank and of Castner. Ammonia is conducted over a mixture of fused sodium and charcoal at 400° , forming sodamide, which at this temperature reacts with carbon, yielding sodium cyanamide, $2\text{NaNH}_2 + \text{C} = \text{CNNNa}_2 + 2\text{H}_2$. On raising the temperature to 800° , $\text{CNNNa}_2 + \text{C} = 2\text{NaCN}$; the yield is said to be nearly the theoretical.

Space considerations forbid reference to further processes, although those for obtaining ferrocyanide from the residues in the purification of coal gas are of great interest. Enough has been said to show that the book is one of definite value to chemists. Dr. LeClerc has made an excellent translation and the book is well printed and illustrated. E. R.

URIC ACID. The Chemistry, Physiology and Pathology of Uric Acid and the Physiologically Important Purin Bodies, with a Discussion of the Metabolism in Gout. By FRANCIS H. MCCRUDDEN. New York: Paul B. Hoeber: 1905. pp. 318. Price, paper \$2.50; canvas, \$3.00 net.

The author here presents the uric acid problem in all of its phases. In dealing with the chemistry of uric acid he begins with its discovery by Scheele, in 1776, and recounts briefly the history of the subject, including the contributions of Liebig and Wöhler, Baeyer, Horbaczewski, Behrend and Fischer. The recent brilliant contributions of physiological chemistry on the synthesis and decomposition of uric acid in birds and mammals are considered in detail. The book includes a consideration of the effect of exercise, diet and drugs on the formation and excretion of uric acid, special stress being laid on those drugs which are used clinically in the treatment of gout. The pharmacological action of the purin derivatives is also discussed. The work of the author in collecting this large amount of widely-scattered literature has been excellently done and the presentation is clear and concise. The admirable bibliography is also a feature of the volume. The

book will be of value to all who are interested in medicine and the medical sciences.

A. S. L.

PHYSICAL CHEMISTRY FOR ELECTRICAL ENGINEERS. By J. L. R. MORGAN, PH.D., Professor of Physical Chemistry in Columbia University. New York: John Wiley & Sons. 1906. Price, \$1.50.

This small book of 230 pages consists of 8 chapters, as follows: Some Fundamental Principles; The General Properties of Gases; Heat and Its Transformation into Other Forms of Energy; Solutions; Chemical Mechanics; Equilibrium in Electrolytes; Electrochemistry; Problems.

In Chapter I. the author insists on the necessity of distinguishing clearly between fact and hypothesis in the matter of atomic and molecular weights, especially at the present time, and to avoid confusion of this character he proposes, throughout the book, to relinquish hypothesis and consider only facts and their generalization. The last chapter consists of a list of 78 problems taken from the author's "Elements of Physical Chemistry." The remaining chapters contain the material presented to the student, the one on electrochemistry being, naturally, much more elaborate than the others.

The book is not intended to be a text-book, its aim is to equip students with the knowledge necessary to understand the current literature in the field of electrochemistry, a branch of science which the author feels has been neglected in their teachings by both physicists and chemists.

The book is clearly written and, on the whole, free from errors, except such minor ones as would be noticeable only to one actively engaged in the particular field treated. The author has made a wise choice of material, but could not the desired end have been reached more satisfactorily by a short treatise on physical chemistry, where the subject would appear in its proper relation to other branches of the science?

J. C. W. F.

THIRD TREATISE ON THE EFFECTS OF BORAX AND BORIC ACID ON THE HUMAN SYSTEM. Being a Critical Review of the Report of DR. H. W. WILEY, Chief of the Bureau of Chemistry of the U. S. Department of Agriculture. By DR. OSCAR LIEBREICH, o. o. Professor der Universität Berlin und Geheimer Medizinalrat. (Translated from the German.) London: J. & A. Churchill. 1906. pp. 70. Price, \$1.75 net.

As stated on the title page, this treatise is merely a critical review of Bulletin No. 84, by Dr. H. W. Wiley. It contains no new data or facts and, therefore, it is only possible to call attention to the book and reserve any remarks until more experimental work is done.

A. S. L.

AMERICAN CHEMICAL JOURNAL

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL, ACETONE AND BINARY MIXTURES OF THESE SOLVENTS.

[FIFTH COMMUNICATION.]

BY HARRY C. JONES AND LEROY MCMASTER.

Four papers¹ have already been published bearing upon the condition of dissolved substances in *mixed solvents*.

PART I.

INTRODUCTION.²

A number of investigations have been carried out in which the electrical conductivities of non-aqueous solutions have been studied, but much less has been done on the conductivities in mixtures of solvents.

¹ Jones and Lindsay: *THIS JOURNAL*, 28, 329 (1902). Jones and Carroll, *Ibid.*, 32, 521 (1904). Jones and Bingham: *Ibid.*, 34, 481 (1905). Jones, Lindsay and Carroll: *Z. physik. Chem.*, 56, 129 (1906).

² This introduction is not a complete historical review of all that has been done upon conductivity or viscosity. In the main, only that work which pertains to mixed solvents has been taken up.

Wakeman,¹ in an elaborate investigation, measured the conductivity of a number of organic acids in mixtures of ethyl alcohol and water, in different proportions. He obtained results which showed that the conductivity became smaller as the amount of alcohol was increased. For the cases studied, the equation,

$$\frac{\Delta}{p(100-p)} = \text{constant},$$

was found to hold, where Δ is the difference between the electrical conductivity of the electrolyte in water and in the mixture, respectively, and p is the per cent of alcohol by volume.

Zelinsky and Krapivin² studied the conductivities of sodium and ammonium bromides and iodides in water, methyl alcohol and a mixture of the two, containing 50 per cent of methyl alcohol; for dilutions from $v = 16$ to $v = 1024$. Their results were of a different character from those previously obtained. The conductivities in the 50 per cent mixture were considerably less than the conductivities in either water or alcohol.

A similar minimum of conductivity was obtained by Cohen,³ working with potassium iodide in mixtures of ethyl alcohol and water. He made a study of the conductivity of this salt in mixtures containing 20, 40, 60, 80 and 99 per cent of the alcohol. The minimum was observed in the 80 per cent mixture at all dilutions greater than $v = 512$.

Cohen concluded, from the observations of Wakeman and from his own, that the relation,

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O} \cdot \text{Alc.}} = \text{constant},$$

holds independent of both concentration and temperature. In other words, the conductivities compared approach a limiting value at the same rate, and either the dissociation is the same in the cases compared, or conductivity is not a direct measure of dissociation in mixtures of alcohol and water. To this latter view Cohen is inclined. The work of Walker and

¹ Z. physik. Chem., 11, 49 (1893).

² *Ibid.*, 21, 35 (1896).

³ *Ibid.*, 25, 31 (1898).

Hambly,¹ Hantzsch,² Tjijmstra³ and Roth⁴ should be mentioned.

Jones and Lindsay⁵ extended the work of Zelinsky and Krapivin and Cohen, by making conductivity measurements of solutions in which the solvents were water, methyl alcohol, ethyl alcohol, propyl alcohol and binary mixtures of these solvents. The salts employed were potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, lithium nitrate and ferric chloride. The result was to show that the occurrence of the minimum is more or less general. The work was, for the most part, done at 0° and 25°. Thus they were able to calculate the temperature coefficients of conductivity of the salts mentioned, in the different solvents, and could also show the influence of temperature on the minimum. They demonstrated that in some cases, although the minimum does not occur at the higher temperature, it appears at the lower. They established the fact that the effect of rise in temperature upon the minimum, is to cause it to shift towards a mixture containing a larger per cent of alcohol. They proposed to account for the conductivity minimum by assuming that each of the two associated solvents diminished the association of the other. Since, according to the theory of Dutoit and Aston, it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes, the cause of the minimum may be stated to be due to a diminution of dissociation and, consequently, a decrease in conductivity.

The above explanation was, later, strengthened by an investigation by Jones and Murray.⁶ From a study of the freezing points of solutions of formic acid, acetic acid and water, and binary mixtures of these substances, they concluded that the association of one solvent is diminished by the presence of another associated solvent.

Jones and Carroll⁷ studied the conductivity of cadmium iodide, sodium iodide, calcium nitrate and hydrochloric acid in

¹ J. Chem. Soc., 71, 61 (1899).

² Ber. d. chem. Ges., 35, 1001 (1902).

³ Proc. Kon. Akad. de Amsterdam, 1903, p. 104.

⁴ Z. physik. Chem., 42, 209 (1903).

⁵ THIS JOURNAL, 28, 329 (1902).

⁶ *Ibid.*, 30, 193 (1903).

⁷ *Ibid.*, 32, 521 (1904).

mixtures of methyl and ethyl alcohols and water. In all cases they observed the minimum at low temperatures.

Noticing the close connection between the viscosity or fluidity of a solvent, and the conductivity of electrolytes when dissolved in this solvent, they took up, in the latter part of their work, a study of this relation. That conductivity and viscosity are related is by no means a new idea, since, as early as 1856, aqueous solutions of copper sulphate were studied, in this connection, by G. Wiedemann.¹

After an investigation of the relations between conductivity and viscosity, Jones and Carroll showed that the explanation of the minimum in conductivity offered by Jones and Lindsay was not sufficient. They proved that the phenomenon was dependent, primarily, upon the decrease in fluidity which results when the components of the solvent are mixed. They also showed that the following hypothesis holds for all cases studied by them: "The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factors of the solvent."

Formulated, this would be expressed by the equations

$$\frac{\mu_v \eta}{x} = \text{constant}, \quad \text{or} \quad \frac{\mu_v \eta}{\alpha} = \text{constant},$$

where x is the association factor and α the dissociation. These formulas become $\mu_v \eta = \text{constant}$ when $\mu_v = \mu \infty$.

This work was next continued by Jones and Bingham² and the relations between the conductivities and viscosities of solutions of lithium nitrate, potassium iodide and calcium nitrate, in various mixtures of acetone with water, methyl alcohol and ethyl alcohol were determined. They worked at 0° and 25° and thus were able to calculate the temperature coefficients of conductivity and of fluidity.

Their results differed from those formerly obtained by the preceding workers, in that the mixtures of acetone with the

¹ Pogg. Ann., 99, 229 (1856).

² THIS JOURNAL, 34, 481 (1905).

alcohols showed a maximum in the conductivity of solutions of certain salts. In the case of mixtures of acetone and water, they observed the minimum previously obtained by other workers.

They measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol and water at 0° and 25° , and also of a few solutions of calcium nitrate at 25° . In the case of acetone and water they found a fluidity minimum, and showed that it was intimately connected with the minimum in conductivity. In the mixtures of acetone and the alcohols they found that the fluidity values obeyed the law of averages. From this fact they concluded that acetone and the alcohols do not form more complex molecular aggregations when mixed, than were originally present before mixing.

After a comprehensive study of all the factors that could influence conductivity, they came to the conclusion that the maximum in conductivity obtained by them was due to a *change in the dimensions of the atmospheres about the ions*. They also showed that the conclusion of Jones and Carroll, that conductivity is proportional to dissociation, was incomplete in that it did not take into consideration possible changes in the size of the ionic spheres.

Jones and Bingham, in their work, showed that the normal curve for viscosities is the hyperbola, and that the normal curve for fluidity is a straight line.

Using the viscosity data of Thorpe and Rodger, Bingham¹ calculated the corresponding values of fluidity for a number of solvents, and plotted the results in curves. He has shown that fluidities alone should be additive and that the normal viscosity curve is a hyperbola, a fact similar to that found by Jones and Bingham.

Some of the recent work on conductivity in non-aqueous solutions should be mentioned. Godlewski² has determined the conductivity of a few weak organic acids in ethyl alcohol and in mixtures of ethyl alcohol and water. In all the cases studied he found that Ostwald's dilution law holds. He also

¹ THIS JOURNAL, 35, 195 (1906).

² J. Chim. Phys. 3, 393 (1905).

determined the conductivity of acetic acid in amyl alcohol and found that it decreases with increasing dilution, until a concentration of about 0.5 N was reached, when it has a minimum value. The dielectric constants of the solutions were found to increase with an increase in dilution.

Dutoit and Levier¹ have determined the conductivity of a few salts in acetone at dilutions as great as $v = 100,000$. They found that the conductivity of the salts became constant at the highest dilutions; and that Kohlrausch's law,

$$\mu_{\infty} = c + a,$$

holds in acetone, where c represents the velocity of the cation and a that of the anion.

Walden² has just published the third part of his investigations on organic solvents. This includes work in methyl and ethyl alcohols and glycol, a number of aldehydes, acid anhydrides and chlorides, organic esters and inorganic acids, nitriles, sulphocyanides and mustard oils, nitro and nitroso compounds, ketones, epichlorhydrin, pyridine, and certain mixtures of some of these solvents.

He finds that for the same electrolyte— $N(C_2H_5)_4I$ —in all of the solvents that were studied, temperature being constant (25°), the product of μ_{∞} times the internal friction is a constant. The product of the internal friction and μ_{∞} for organic solvents was shown to be independent of the nature of the solvent and of the temperature.

In reference to the relation pointed out by Jones and Carroll, to which Walden refers,³ it should be stated that Jones and Carroll tested this relation for only a limited number of solvents. For these it held fairly satisfactorily. The concentrations used were the simplest possible, *i. e.*, a molecule of the substance in so many molecules of the solvent. In their calculations the association factors of the several solvents were not introduced, since this was the very point to be tested.

Our work was undertaken as an extension of the work of Jones and Carroll on the one hand, and of that of Jones and

¹ J. Chim. Phys. **3**, 435 (1905).

² Z. physik. Chem., **55**, 207 (1906).

³ *Ibid.*, **55**, 213 (1906).

Bingham on the other. It will be recalled that Jones and Carroll investigated the relations between conductivity and viscosity of salts in water, methyl and ethyl alcohols and binary mixtures of these solvents; while Jones and Bingham pointed out the relation between conductivity and viscosity of certain salts in mixtures of acetone with methyl and ethyl alcohols and water.

We have worked with water, methyl alcohol, ethyl alcohol, acetone and 17 different binary mixtures of these solvents. The salts studied were lithium bromide and cobalt chloride.

PART II.

EXPERIMENTAL.

Apparatus.

(a) *Conductivity.*—The Kohlrausch method of measuring conductivity, with a Wheatstone bridge, telephone receiver and induction coil, was employed. The bridge wire was of "manganin" and was calibrated before beginning the work by the method of Strouhal and Barus.¹

The resistance coils, manufactured by Leeds & Co., were tested and found to be accurate to within 0.04 per cent.

The conductivity cells were of the form used by Jones and Bingham.² In order to work with the alcohols and acetone, it was necessary to use cells of this form. They were made of hard glass, with ground-glass stoppers. The glass tubes carrying the platinum electrodes were sealed into both the upper and lower walls of the stopper. By using such cells, the presence of rubber or wax, which would be dissolved by the solutions, was avoided. They also prevent evaporation of the more volatile solvents, and protect the anhydrous alcohols and acetone from the moisture of the baths and air.

The electrodes were treated in the manner recommended by Whetham.³ They were first coated with platinum black and then heated in the flame of a blast-lamp. Electrodes covered with platinum black absorb a small amount of salt from the

¹ Wied. Ann., 10, 326 (1880).

² THIS JOURNAL, 34, 493 (1905).

³ Phil. Trans., 94 [A], 321 (1900).

solution and give up some of it again when water, or a more dilute solution is placed in the cell. The gray platinum formed by the heating process does not absorb an appreciable amount of salt, and the oxidizing action of platinum black is also avoided by this treatment.

The zero bath consisted of an inner and outer vessel. The inner vessel and the space between the two were filled with finely crushed, pure ice, moistened with distilled water. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine, or a Rabe water turbine. The Ostwald thermoregulator was used. The thermometers employed were accurate to a tenth of a degree. Burettes and flasks were carefully calibrated, according to the method of Morse and Blalock.¹

(b) *Viscosity*.—The apparatus used was exactly of the form described by Ostwald and Luther.² A fixed volume of the liquid, the viscosity of which was to be measured, was introduced into the viscometer. The liquid was raised to the mark above the bulb by means of air pressure, the air being dried with calcium chloride, or with concentrated sulphuric acid. The pressure was then released by means of a Mohr pinch-cock on a thick-walled rubber tube. The time of flow through the capillary tube was determined by means of a stop-watch, reading to two-tenths of a second.

We are indebted to Mr. Arthur C. Macy, jeweler, for the loan of a Waltham stop-watch.

In order to calculate the viscosity, it is necessary to measure the specific gravity of the solution. For this purpose we used the pycnometer employed by Jones and Bingham³ in their work. The pycnometer was so constructed as to allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

A large battery jar, filled with finely crushed ice moistened with water, was used for the zero bath. The ice was frequently renewed to keep the temperature constant. For the

¹ THIS JOURNAL, 16, 479 (1894).

² Physiko.-chemische Messungen, II. Aufl., p. 260.

³ THIS JOURNAL, 34, 495 (1905).

25° bath a beaker holding 5 liters was used. The bath was stirred by means of a hot-air engine, the temperature being kept at 25°. It did not vary more than a tenth of a degree.

Solvents.

Water.—The water used in this work was purified according to the following method: Ordinary distilled water was first distilled from potassium bichromate and sulphuric acid. This water was redistilled from acidified potassium bichromate and then from barium hydroxide. Water thus purified gave a conductivity of 1×10^{-6} at 0° and from $1.5-2.0 \times 10^{-6}$ at 25°.

Methyl Alcohol.—The methyl alcohol used was the best commercial article which could be obtained. It was first boiled with calcium oxide for several days, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate, using a Linnemann fractionating head. Care was always taken to keep it free from moisture. The first and last portions of the distillate were discarded. The mean value of the conductivity was 1.1×10^{-6} at 0° and 2×10^{-6} at 25°.

Ethyl Alcohol.—The ethyl alcohol was the best article commercially obtainable, and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 0.6×10^{-6} at 0° and 1.5×10^{-6} at 25°.

Acetone.—The acetone was dried over fused calcium chloride for weeks and distilled with a Linnemann fractionating head. Its conductivity was 0.4×10^{-6} at 0° and 0.6×10^{-6} at 25°.

Solutions.

In making up mixtures of solvents, " x " cc. of an alcohol or of acetone were diluted to 100 cc. Such a solution was designated as a mixture of " x per cent alcohol" or " x per cent acetone." Since acetone has a large coefficient of expansion, it was necessary to make up the mixtures at the same temperature (18°). The alcohol or acetone was always brought to this temperature before making up the mixture.

In making up the mother solution the exact amount of the salt was weighed into a measuring flask and, after addition of

a portion of the solvent, the substance was dissolved and the flask filled to the mark. Since heat was generated and there was a rise in temperature, the solution was brought to the designated temperature before diluting to the mark. The various concentrations were obtained by successive dilution, the mother solution being the starting point. Where the quantity to be used was too small to be measured with accuracy, one of the intermediate solutions was taken as a starting point for further dilution.

Conductivity Measurements.

In all determinations of conductivity from 3 to 5 different resistances were used. The values for the molecular conductivity (μ_v), given in the tables, are, therefore, the mean of several determinations. The determination of the cell constants was carried out by the method employed by Jones and West.¹ Cells calibrated in this manner gave very accurate results. The constants were checked at frequent intervals. After being used the cells were not allowed to remain in contact with the solution, because small quantities of salt are absorbed by the electrodes. Nor were they allowed to remain empty after being dried out with alcohol and ether, since acetic acid is formed by the action of the platinum on the alcohol and ether in the presence of air, but they were always filled with pure distilled water when not in use.

Solutions of potassium chloride, 0.02 N and 0.002 N, were used in determining the cell constants. The conductivity of the former was taken as 129.7, at 25°; 136.5 at 25° being taken as the value of μ_v for the 0.002 N solution of potassium chloride.

In the following tables v = number of liters of solution containing a gram-molecular weight of the salt; μ_v 0° = molecular conductivity at 0°; μ_v 25° = molecular conductivity at 25°.

The temperature coefficients are obtained by dividing the increase in the conductivity per degree by the conductivity at the lower temperature. The formula, that was applied, is

¹ THIS JOURNAL, 34, 357 (1905).

$$\frac{\mu_v 25^\circ - \mu_v 0^\circ}{25} \cdot \frac{1}{\mu_v 0^\circ}.$$

LITHIUM BROMIDE.

The lithium bromide used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 159° , after which it was kept in a desiccator. Whenever the salt was exposed to the air the operation of drying to constant weight was repeated.

Table I.—Conductivity of Lithium Bromide in Water at 0° and 25° .

<i>v.</i>	$\mu_v 0^\circ$.	$\mu_v 25^\circ$.	Temperature coefficients.
2	42.09	76.17	0.0324
5	45.33	83.33	0.0335
10	47.25	86.09	0.0329
50	51.43	95.62	0.0344
100	51.92	96.41	0.0342
200	53.27	99.51	0.0347
400	53.71	100.34	0.0347
800	55.45	104.81	0.0356
1600	56.12	106.23	0.0357

Table II.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25° .

<i>v.</i>	$\mu_v 0^\circ$.	$\mu_v 25^\circ$.	Temperature coefficients.
2	24.46	49.86	0.0415
5	26.57	54.90	0.0426
10	27.52	57.46	0.0435
50	30.04	63.69	0.0448
100	30.50	64.78	0.0450
200	31.24	66.25	0.0448
400	31.65	66.65	0.0442
800	32.87	68.83	0.0438
1600	33.07	69.24	0.0437

Table III.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	18.42	37.01	0.0404
5	20.57	41.58	0.0408
10	21.71	43.99	0.0410
50	24.24	49.46	0.0416
100	24.40	50.27	0.0424
200	25.16	51.74	0.0423
400	25.96	53.24	0.0420
800	26.42	54.48	0.0425
1600	26.91	55.15	0.0420

Table IV.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	19.51	33.66	0.0290
5	21.67	38.31	0.0307
10	23.50	41.99	0.0314
50	27.05	48.68	0.0320
100	27.73	49.98	0.0321
200	28.92	52.29	0.0323
400	29.55	53.56	0.0325
800	30.22	55.29	0.0332
1600	31.35	57.59	0.0335

Table V.—Conductivity of Lithium Bromide in Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	22.02	31.35	0.0169
5	30.55	42.57	0.0157
10	35.92	50.21	0.0159
50	46.48	64.92	0.0159
100	49.36	69.19	0.0161
200	52.51	73.62	0.0161
400	55.18	78.25	0.0167
800	57.45	82.56	0.0175
1600	57.63	83.64	0.0181

Table VI.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	42.09	24.46	18.42	19.51	22.02
5	45.33	26.57	20.57	21.67	30.55
10	47.25	27.52	21.71	23.50	35.92
50	51.43	30.04	24.24	27.05	46.48
100	51.92	30.50	24.40	27.73	49.36
200	53.27	31.24	25.16	28.92	52.51
400	53.71	31.65	25.96	29.55	55.18
800	55.45	32.87	26.42	30.22	57.45
1600	56.12	33.07	26.91	31.35	57.63

Table VII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	76.17	49.86	37.01	33.66	31.35
5	83.33	54.90	41.58	38.31	42.57
10	86.09	57.46	43.99	41.99	50.21
50	95.62	63.69	49.46	48.68	64.92
100	96.41	64.78	50.27	49.98	69.19
200	99.51	66.25	51.74	52.29	73.62
400	100.34	66.65	53.24	53.56	78.25
800	104.81	68.83	54.48	55.29	82.56
1600	106.23	69.24	55.15	57.59	83.64

Table VIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Methyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	0.0324	0.0415	0.0404	0.0290	0.0169
5	0.0335	0.0426	0.0408	0.0307	0.0157
10	0.0329	0.0435	0.0410	0.0314	0.0159
50	0.0344	0.0448	0.0416	0.0320	0.0159
100	0.0342	0.0450	0.0424	0.0321	0.0161
200	0.0347	0.0448	0.0423	0.0323	0.0161
400	0.0347	0.0442	0.0420	0.0325	0.0167
800	0.0356	0.0438	0.0425	0.0332	0.0175
1600	0.0357	0.0437	0.0420	0.0335	0.0181

Tables I. to VIII. (Figs. I. and II.) show that lithium bromide, in mixtures of methyl alcohol and water, gives a pronounced minimum in conductivity. The minimum is more marked at 0° than at 25° . At 25° the minimum occurs in the 75 per cent mixture up to $v = 100$. Beyond this dilution the

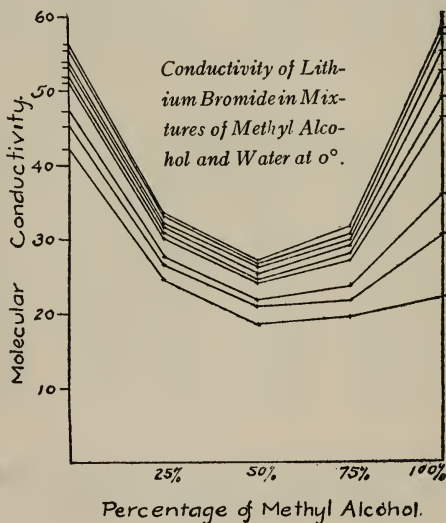


Fig. I.

minimum occurs solely in the 50 per cent mixture. At 0° the minimum appears in the 50 per cent mixture alone. We also notice that at 0° the values of μ_v for the pure methyl alcohol at the higher dilutions, exceed the values of μ_v for the corresponding aqueous solutions.

These points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

The temperature coefficients of conductivity increase with the dilution, and they are also greater in the mixtures than in

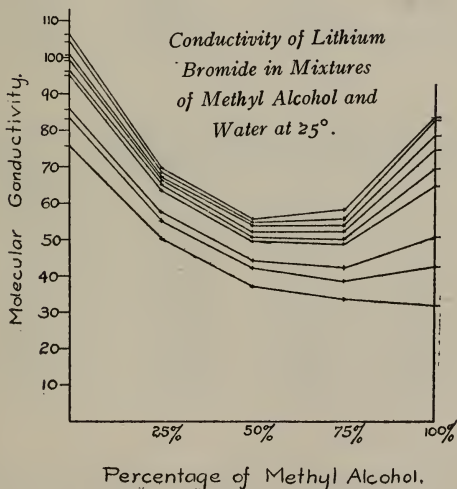


Fig. II.

the pure solvents, the maximum appearing in the 25 per cent mixture. The temperature coefficients of conductivity of salts in water generally increase with the dilution, as Jones¹ has pointed out in a recent article.

¹ THIS JOURNAL, 35, 445 (1906).

Table IX.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	17.82	41.21	0.0525
5	18.92	45.03	0.0552
10	19.66	47.05	0.0557
50	21.60	52.52	0.0572
100	21.67	52.58	0.0570
200	22.09	54.37	0.0584
400	22.50	54.41	0.0567
800	24.51	56.46	0.0521
1600	25.72	57.10	0.0448

Table X.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients
2	11.70	27.50	0.0540
5	12.48	29.51	0.0546
10	12.62	31.41	0.0595
50	13.71	35.41	0.0633
100	13.98	36.12	0.0633
200	14.34	37.26	0.0639
400	14.96	38.39	0.0626
800	15.77	39.94	0.0613
1600	16.06	40.01	0.0596

Table XI.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	9.20	18.96	0.0424
5	10.55	22.11	0.0438
10	11.59	24.26	0.0437
50	11.87	25.62	0.0463
100	12.14	26.29	0.0466
200	12.77	27.66	0.0466
400	13.13	28.62	0.0472
800	13.62	29.78	0.0474
1600	13.83	29.91	0.0465

Table XII.—Conductivity of Lithium Bromide in Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
2	6.11	10.18	0.0266
5	8.67	14.00	0.0246
10	10.55	17.22	0.0253
50	14.40	23.28	0.0247
100	15.69	25.57	0.0252
200	17.29	28.26	0.0254
400	18.55	30.32	0.0254
800	19.71	31.73	0.0244
1600	20.79	33.36	0.0242

Table XIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 0°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	42.09	17.82	11.70	9.20	6.11
5	45.33	18.92	12.48	10.55	8.67
10	47.25	19.66	12.62	11.59	10.55
50	51.43	21.60	13.71	11.87	14.40
100	51.92	21.67	13.98	12.14	15.69
200	53.27	22.09	14.34	12.77	17.29
400	53.71	22.50	14.96	13.13	18.55
800	55.45	24.51	15.77	13.62	19.71
1600	56.12	25.72	16.06	13.83	20.79

Table XIV.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 25°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	76.17	41.21	27.50	18.96	10.18
5	83.83	45.03	29.51	22.11	14.00
10	86.09	47.05	31.41	24.26	17.22
50	95.62	52.52	35.41	25.62	23.28
100	96.41	52.58	36.12	26.29	25.57
200	99.51	54.37	37.26	27.66	28.26
400	100.34	54.41	38.39	28.62	30.32
800	104.81	56.46	39.94	29.78	31.73
1600	106.23	57.10	40.01	29.91	33.36

Table XV.—Comparison of the Temperature Coefficientsof Conductivity of Lithium Bromide in Mixtures of Ethyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	0.0324	0.0525	0.0540	0.0424	0.0266
5	0.0335	0.0552	0.0546	0.0438	0.0246
10	0.0329	0.0557	0.0595	0.0437	0.0253
50	0.0344	0.0572	0.0633	0.0463	0.0247
100	0.0342	0.0570	0.0633	0.0466	0.0252
200	0.0347	0.0584	0.0639	0.0466	0.0254
400	0.0347	0.0567	0.0626	0.0472	0.0254
800	0.0356	0.0521	0.0613	0.0474	0.0244
1600	0.0357	0.0448	0.0596	0.0465	0.0242

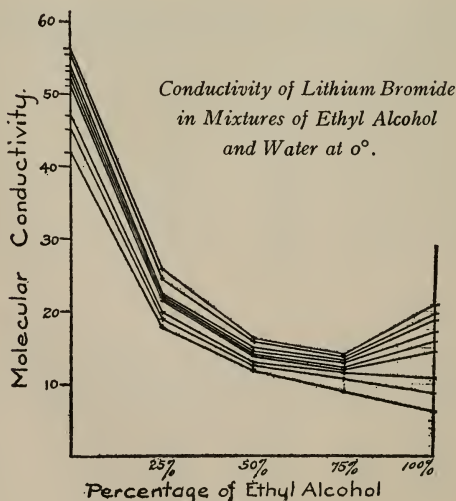
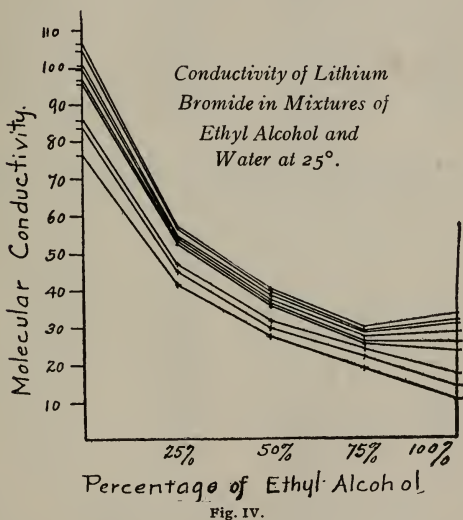


Fig. III.

Tables IX. to XV. (Figs. III. and IV.) show that lithium bromide, in mixtures of ethyl alcohol and water, also gives a

minimum in conductivity. At high concentrations the minimum does not appear, either at 0° or at 25° . At both temperatures the minimum appears only in the 75 per cent mixture. At 0° the minimum begins with $v = 50$, at 25° it be-



gins at $v = 200^\circ$. It is to be noticed that the minimum is more marked at the lower temperature, being very slight at 25° .

The temperature coefficients in ethyl alcohol are almost constant. This same fact was found by Jones and Bingham¹ in the case of calcium nitrate. The temperature coefficients are greater in the mixtures than in the pure solvents, the maximum appearing in the 50 per cent mixture.

¹ THIS JOURNAL, 34, 529 (1905).

Table XVI.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	8.59	13.51	0.0229
5	12.55	19.08	0.0208
10	15.17	22.97	0.0206
50	21.07	31.56	0.0199
100	22.70	34.55	0.0209
200	24.50	37.61	0.0214
400	26.08	40.03	0.0214
800	26.94	41.82	0.0221
1600	29.08	45.07	0.0220

Table XVII.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	12.22	18.37	0.0201
5	17.38	25.54	0.0188
10	21.03	30.72	0.0184
50	28.69	41.81	0.0183
100	30.42	44.48	0.0185
200	32.95	48.86	0.0193
400	34.76	51.31	0.0190
800	35.83	53.29	0.0195
1600	37.53	55.74	0.0194

Table XVIII.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	16.46	24.22	0.0188
5	23.34	33.38	0.0172
10	27.71	39.60	0.0171
50	37.02	52.80	0.0170
100	38.96	55.92	0.0174
200	41.64	60.03	0.0176
400	44.21	63.76	0.0177
800	46.51	66.73	0.0174
1600	49.57	71.37	0.0176

Table XIX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol at 0°.

v.	C ₂ H ₅ OH.	25 per cent CH ₃ OH.	50 per cent CH ₃ OH.	75 per cent CH ₃ OH.	CH ₃ OH.
2	6.11	8.59	12.22	16.46	22.02
5	8.67	12.55	17.38	23.34	30.55
10	10.55	15.17	21.03	27.71	35.92
50	14.40	21.07	28.69	37.02	46.48
100	15.69	22.70	30.42	38.96	49.36
200	17.27	24.50	32.95	41.64	52.51
400	18.55	26.08	34.76	44.21	55.18
800	19.71	26.94	35.83	46.51	57.45
1600	20.79	29.08	37.53	49.57	57.63

Table XX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol at 25°.

v.	C ₂ H ₅ OH.	25 per cent CH ₃ OH.	50 per cent CH ₃ OH.	75 per cent CH ₃ OH.	CH ₃ OH.
2	10.18	13.51	18.37	24.22	31.35
5	14.00	19.08	25.54	33.38	42.57
10	17.22	22.97	30.72	39.60	50.21
50	23.28	31.56	41.81	52.80	64.92
100	25.57	34.55	44.48	55.92	69.19
200	28.26	37.61	48.86	60.03	73.62
400	30.32	40.03	51.31	63.76	78.25
800	31.73	41.82	53.29	66.73	82.56
1600	33.36	45.07	55.74	71.37	83.64

Table XXI.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol from 0° to 25°.

v.	C ₂ H ₅ OH.	25 per cent CH ₃ OH.	50 per cent CH ₃ OH.	75 per cent CH ₃ OH.	CH ₃ OH.
2	0.0266	0.0229	0.0201	0.0188	0.0169
5	0.0246	0.0208	0.0188	0.0172	0.0157
10	0.0253	0.0206	0.0184	0.0171	0.0159
50	0.0247	0.0199	0.0183	0.0170	0.0159
100	0.0252	0.0209	0.0185	0.0174	0.0161
200	0.0254	0.0214	0.0193	0.0176	0.0161
400	0.0254	0.0214	0.0190	0.0177	0.0167
800	0.0244	0.0221	0.0195	0.0174	0.0175
1600	0.0242	0.0220	0.0194	0.0176	0.0181

Tables XVI. to XXI. (Figs. V. and VI.) show that lithium bromide, in mixtures of methyl and ethyl alcohols, gives no minimum in conductivity. In fact, the conductivity values

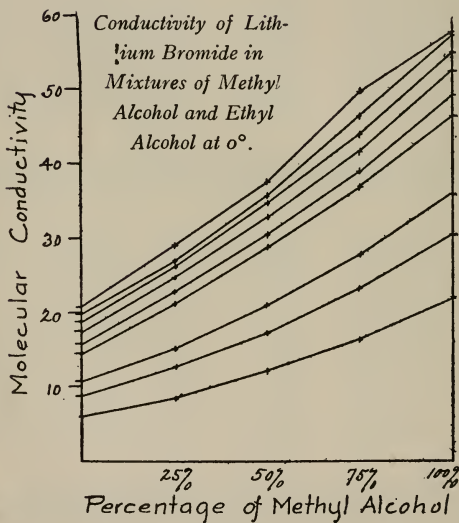


Fig. V.

for the solutions in the mixed solvent approach the mean value of the conductivities in the pure solvents. The conductivity curves at the high concentrations show a slight sagging at both temperatures, but beyond $v = 50$ the curves are nearly straight lines.

This same fact has been observed by others¹ working with mixtures of methyl and ethyl alcohols. The temperature coefficients obey, approximately, the law of averages.

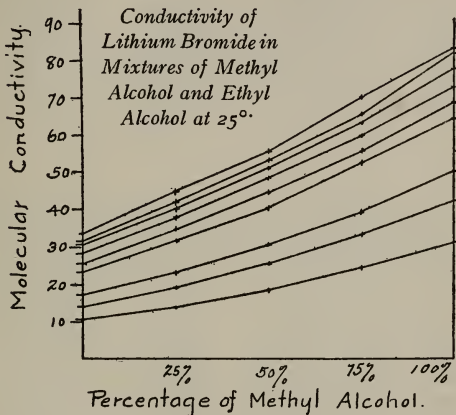


Fig. VI.

Table XXII.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.58	56.23	0.0415
10	28.82	59.71	0.0429
50	31.49	65.64	0.0434
100	31.60	65.82	0.0433
200	32.29	67.88	0.0441
400	32.98	68.69	0.0433
800	35.18	70.25	0.0399
1600	35.70	71.47	0.0401

¹ Jones and Lindsay : *Loc. cit.* Jones and Carroll : *Loc. cit.*

Table XXIII.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	20.37	41.82	0.0421
10	21.70	45.16	0.0432
50	24.81	51.95	0.0437
100	25.03	52.46	0.0438
200	26.10	54.64	0.0437
400	26.81	56.44	0.0442
800	27.07	57.54	0.0430
1600	28.34	59.28	0.0437

Table XXIV.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	17.40	31.47	0.0323
10	20.40	36.49	0.0315
50	25.76	46.77	0.0326
100	27.29	49.87	0.0331
200	28.87	52.87	0.0332
400	30.10	55.53	0.0338
800	30.20	56.46	0.0348
1600	31.65	61.10	0.0372

Table XXV.—Conductivity of Lithium Bromide in Acetone at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	9.35	10.82	0.00629
10	11.91	14.08	0.00729
50	22.36	26.77	0.00789
100	28.86	34.52	0.00784
200	37.33	47.45	0.01080
400	48.28	57.96	0.00802
800	59.42	72.16	0.00858
1600	70.89	85.90	0.00847

Table XXVI.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	45.33	27.58	20.37	17.40	9.35
10	47.25	28.82	21.70	24.00	11.91
50	51.43	31.49	24.81	25.76	22.36
100	51.92	31.60	25.03	27.29	28.86
200	53.27	32.29	26.10	28.87	37.33
400	53.71	32.98	26.81	30.10	48.28
800	55.45	35.18	27.07	30.20	59.42
1600	56.12	35.71	28.34	31.65	70.89

Table XXVII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	83.33	56.23	41.82	31.47	10.82
10	86.09	59.71	45.16	36.49	14.80
50	95.61	65.64	51.95	46.77	26.77
100	96.41	65.82	52.46	49.87	34.52
200	99.51	67.88	54.64	52.87	47.45
400	100.34	68.69	56.44	55.53	57.96
800	104.81	70.25	57.54	56.46	72.16
1600	106.23	71.47	59.28	61.10	85.90

Table XXVIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0335	0.0415	0.0421	0.0323	0.00629
10	0.0329	0.0429	0.0432	0.0315	0.00729
50	0.0344	0.0434	0.0437	0.0326	0.00789
100	0.0342	0.0433	0.0438	0.0331	0.00784
200	0.0347	0.0441	0.0437	0.0332	0.01080
400	0.0347	0.0433	0.0442	0.0338	0.00802
800	0.0356	0.0399	0.0430	0.0348	0.00858
1600	0.0357	0.0401	0.0437	0.0372	0.00847

Tables XXII. to XXVIII. (Figs. VII. and VIII.) for lithium bromide, in mixtures of acetone and water, give the minimum which is exhibited in mixtures of the alcohols and water

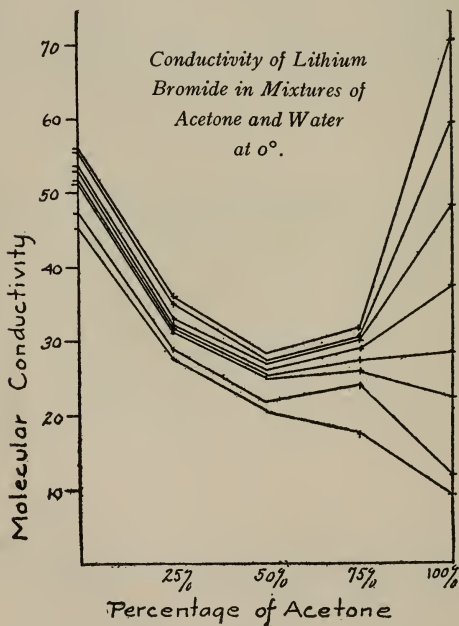


Fig. VII.

under similar circumstances. The minimum is more marked at the lower temperature. The curves diverge from each other rapidly between the 75 per cent mixture and pure ace-

tone, at both temperatures. This seems to indicate that the addition of small amounts of water greatly increases the dissociation. It is also to be noticed that, at the lower temperature, the values of μ_v for the pure acetone at the higher dilu-

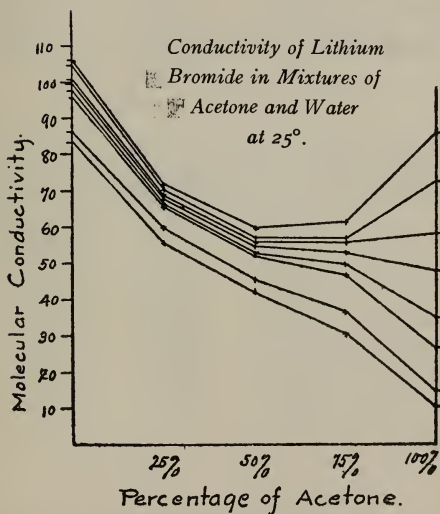


Fig. VIII.

tions exceed those of μ_v for the corresponding water solutions. A similar phenomenon was noticed in the methyl alcohol and water solutions.

In pure acetone the temperature coefficients increase with the dilution. In the mixtures the increase is very small.

Table XXIX.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	29.65	40.04	0.0140
10	35.03	47.57	0.0143
50	46.71	63.44	0.0143
100	49.68	67.40	0.0142
200	53.28	73.81	0.0154
400	56.45	78.11	0.0153
800	58.91	81.55	0.0154
1600	60.38	83.53	0.0153

Table XXX.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.99	35.37	0.0105
10	34.27	42.32	0.00939
50	48.65	61.77	0.0108
100	52.67	68.29	0.0118
200	57.69	74.13	0.0114
400	61.74	79.77	0.0117
800	64.70	85.57	0.0129
1600	67.02	89.45	0.0134

Table XXXI.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	23.36	30.06	0.0115
10	29.77	38.15	0.0112
50	48.45	61.89	0.0111
100	55.00	70.87	0.0115
200	62.74	80.63	0.0114
400	72.25	91.17	0.0105
800	82.20	100.28	0.0088
1600	84.15	106.14	0.0104

Table XXXII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	30.55	29.65	27.99	23.36	9.35
10	35.92	35.03	34.27	29.77	11.91
50	46.48	46.71	48.65	48.45	22.36
100	49.36	49.68	52.67	55.00	28.86
200	52.51	53.28	57.69	62.74	37.33
400	55.18	56.45	61.74	72.25	48.28
800	57.45	58.91	64.70	82.20	59.42
1600	57.63	60.38	67.02	84.15	70.89

Table XXXIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	42.57	40.04	35.37	30.06	10.82
10	50.21	47.57	42.32	38.15	14.08
50	64.92	63.44	61.77	61.89	26.77
100	69.19	67.40	68.29	70.87	34.52
200	73.62	73.81	74.13	80.63	47.45
400	78.25	78.11	79.77	91.17	57.96
800	82.56	81.55	85.57	100.28	72.16
1600	83.64	83.53	89.45	106.14	85.90

Table XXXIV.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0157	0.0140	0.0105	0.0115	0.00629
10	0.0159	0.0143	0.00939	0.0112	0.00729
50	0.0159	0.0143	0.0108	0.0111	0.00789
100	0.0161	0.0142	0.0118	0.0115	0.00784
200	0.0161	0.0154	0.0114	0.0114	0.01080
400	0.0167	0.0153	0.0117	0.0105	0.00802
800	0.0175	0.0154	0.0129	0.0088	0.00858
1600	0.0181	0.0153	0.0134	0.0104	0.00847

Tables XXIX. to XXXIV. (Figs. IX. and X.) for lithium bromide, in mixtures of acetone and methyl alcohol, give a maximum in conductivity in the 75 per cent mixture at both

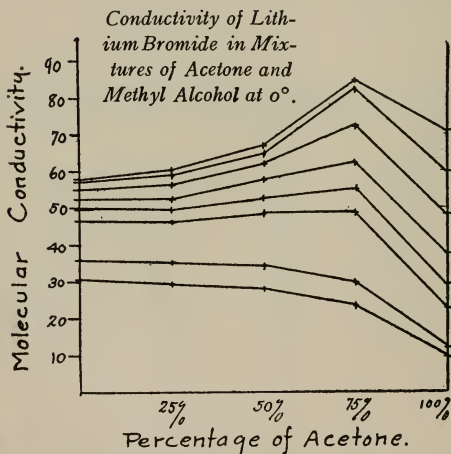


Fig. IX.

temperatures. The maximum is increased by rise in temperature. This same phenomenon was found by Jones and Bing-

ham, working with lithium nitrate in mixtures of acetone and methyl alcohol. It will be recalled that we obtained a mini-

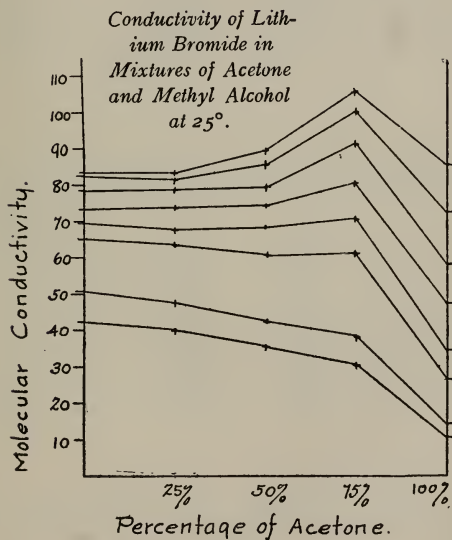


Fig. X.

mum conductivity with this salt in mixtures of the alcohols and water.

Table XXXV.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	11.80	16.94	0.0174
10	14.72	20.91	0.0168
50	21.70	31.00	0.0171
100	23.70	34.38	0.0180
200	26.38	38.27	0.0180
400	28.28	41.74	0.0190
800	28.88	42.97	0.0195
1600	29.21	44.24	0.0206

Table XXXVI.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.70	19.38	0.0122
10	19.23	25.75	0.0135
50	30.25	39.36	0.0120
100	34.50	45.12	0.0123
200	39.20	52.76	0.0138
400	43.83	59.26	0.0141
800	46.92	64.33	0.0148
1600	50.98	71.22	0.0159

Table XXXVII.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.48	18.07	0.00992
10	19.16	23.23	0.00850
50	33.20	40.08	0.00829
100	39.32	48.94	0.00978
200	47.31	58.01	0.00905
400	55.55	68.28	0.00917
800	61.20	77.57	0.01070
1600	66.28	83.36	0.01030

Table XXXVIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	8.67	11.8	14.70	14.48	9.35
10	10.55	14.72	19.23	19.16	11.91
50	14.40	21.70	30.25	33.20	22.36
100	15.69	23.70	34.50	39.32	28.86
200	17.29	26.38	39.20	47.31	37.33
400	18.55	28.28	43.83	55.55	48.28
800	19.71	28.88	46.92	61.20	59.42
1600	20.79	29.21	50.98	66.28	70.89

Table XXXIX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.00	16.94	19.38	18.07	10.82
10	17.22	20.91	25.75	23.23	14.08
50	23.28	31.00	39.36	40.08	26.77
100	25.57	34.38	45.12	48.94	34.52
200	28.26	38.27	52.76	58.01	47.45
400	30.32	41.74	59.26	68.28	57.96
800	31.73	42.97	64.33	77.57	72.16
1600	33.36	44.24	71.22	83.36	85.90

Table XL.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0246	0.0174	0.0122	0.00992	0.00629
10	0.0253	0.0168	0.0135	0.00850	0.00729
50	0.0247	0.0171	0.0120	0.00829	0.00789
100	0.0252	0.0180	0.0123	0.00978	0.00784
200	0.0254	0.0180	0.0138	0.00905	0.01080
400	0.0254	0.0190	0.0141	0.00917	0.00802
800	0.0244	0.0195	0.0148	0.01070	0.00858
1600	0.0242	0.0206	0.0159	0.01030	0.00847

Tables XXXV. to XL. (Figs. XI. and XII.) for lithium bromide, in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this salt

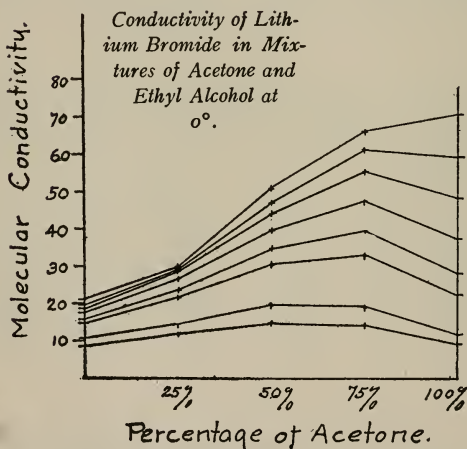


Fig. XI.

in mixtures of acetone and methyl alcohol. The values for μ_v in acetone are greater than the corresponding values in the pure ethyl alcohol at practically all dilutions.

The temperature coefficients increase slightly with the increase in dilution. The values are highest in ethyl alcohol,

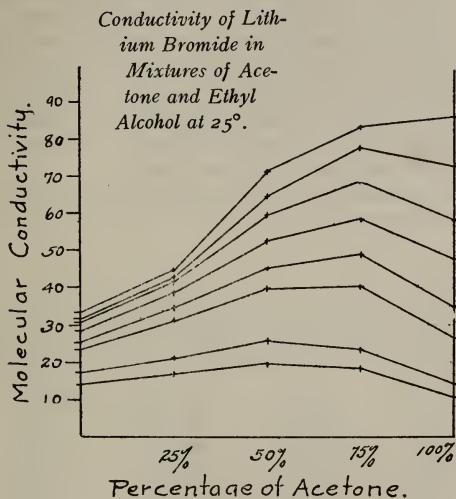


Fig. XII.

from which there is a regular gradation to the values of pure acetone.

COBALT CHLORIDE.

The cobalt chloride used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. This salt cannot be dehydrated in contact with the air, and special precautions must be taken to prevent the formation of the oxychloride. The salt containing 6 molecules of water was first placed over concentrated sulphuric acid, in a vacuum desiccator, for several days. It was thus deprived of part of its water of crystallization. It was then placed in an air-bath and dried at 140°–150°, in a stream of dry hydrochloric acid gas. The salt was subsequently kept in a vacuum desiccator over sul-

phuric acid and potassium hydroxide. It gave no test for free hydrochloric acid, and possessed a pale, sky-blue color.

Cobalt chloride, dissolved in methyl and ethyl alcohols and acetone, gives rise to a number of color phenomena. These changes have been extensively studied by many investigators. Spectroscopic observations concerning the color changes of cobalt chloride in water, methyl and ethyl alcohol, acetone and binary mixtures of these solvents, are now being carried out in this laboratory by Jones and Uhler. The results of this work will be published in the near future.

Hydrolysis probably comes into play, to some extent, in the more dilute water solutions.

Table XLI.—Conductivity of Cobalt Chloride in Water at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
10	86.42	156.36	0.0324
50	104.31	189.27	0.0326
100	109.27	197.41	0.0322
200	113.73	213.40	0.0350
400	115.87	219.63	0.0358
800	116.71	220.04	0.0354
1600	117.40	221.50	0.0355

Table XLII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
10	43.97	92.35	0.0440
50	52.02	110.24	0.0447
100	52.39	112.95	0.0462
200	57.20	126.60	0.0485
400	57.99	125.17	0.0463
800	60.14	127.46	0.0447
1600	61.98	133.98	0.0472

Table XLIII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	32.94	65.85	0.0400
50	39.96	82.44	0.0425
100	41.39	85.58	0.0427
200	44.95	92.90	0.0427
400	46.15	96.35	0.0435
800	48.51	100.54	0.0429
1600	51.40	104.19	0.0411

Table XLIV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	27.40	49.58	0.0324
50	37.45	61.58	0.0258
100	38.07	66.17	0.0296
200	43.16	76.01	0.0304
400	45.54	77.82	0.0283
800	48.55	80.51	0.0263
1600	51.39	84.39	0.0257

Table XLV.—Conductivity of Cobalt Chloride in Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	33.46	41.78	0.00995
50	51.76	65.22	0.01040
100	60.89	76.08	0.00998
200	70.45	87.37	0.00961
400	75.64	99.96	0.01280
800	86.57	117.18	0.01410
1600	95.54	133.33	0.01580

Table XLVI.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	86.42	43.97	32.94	27.40	33.46
50	104.31	52.02	39.96	37.45	51.76
100	109.27	52.39	41.39	38.07	60.89
200	113.73	57.20	44.95	43.16	70.45
400	115.87	57.99	46.15	45.54	75.64
800	116.71	60.14	48.51	48.55	86.57
1600	117.40	61.98	51.40	51.39	95.54

Table XLVII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	156.36	92.35	65.85	49.58	41.780
50	189.27	110.24	82.44	61.58	65.220
100	197.41	112.95	85.58	66.17	76.080
200	213.40	126.60	92.90	76.01	87.370
400	219.63	125.17	96.35	77.82	99.960
800	220.04	127.46	100.54	80.51	117.18
1600	221.50	133.98	104.19	84.39	133.33

Table XLVIII.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0324	0.0440	0.0400	0.0324	0.00995
50	0.0326	0.0447	0.0425	0.0258	0.01040
100	0.0322	0.0462	0.0427	0.0296	0.00998
200	0.0350	0.0485	0.0427	0.0304	0.00961
400	0.0358	0.0463	0.0435	0.0283	0.01280
800	0.0354	0.0447	0.0429	0.0263	0.01410
1600	0.0355	0.0472	0.0411	0.0257	0.01580

Tables XLI. to XLVIII. (Figs. XIII. and XIV.) for cobalt chloride, in mixtures of methyl alcohol and water, show a minimum in conductivity at both temperatures. It should be noticed that the minimum, which occurs in the 75 per cent

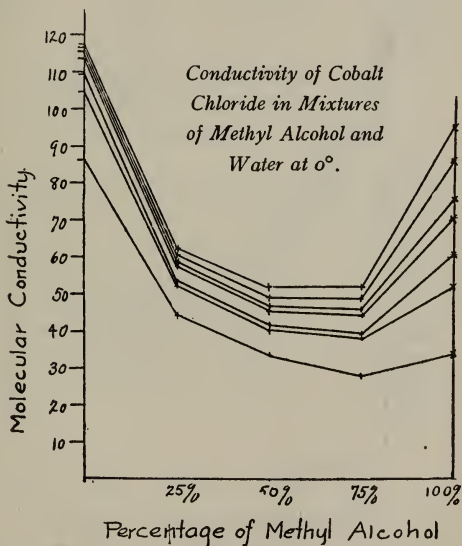


Fig. XIII.

mixture at both temperatures, is more marked at 25° than at 0°. In the case of lithium bromide, in mixtures of methyl alcohol and water, the minimum appeared more pronounced at the lower temperature. Between the 75 per cent mixture and

pure methyl alcohol the curves diverge rapidly from each other. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

The temperature coefficients increase with the dilution,

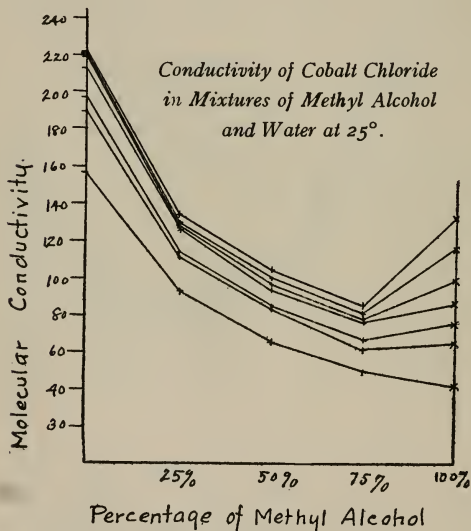


Fig. XIV.

especially in the water and pure methyl alcohol solutions. The temperature coefficients are greater in the mixtures than in the pure solvents, reaching a maximum in the 25 per cent mixture.

Table XLIX.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	30.53	73.68	0.0565
50	33.74	85.65	0.0615
100	34.64	87.60	0.0611
200	35.64	94.42	0.0660
400	37.63	97.64	0.0638
800	41.89	101.33	0.0568
1600	42.42	103.86	0.0579

Table L.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	18.17	44.75	0.0585
50	21.55	55.21	0.0625
100	22.46	57.41	0.0622
200	23.83	63.42	0.0664
400	24.76	64.00	0.0634
800	26.46	69.34	0.0648
1600	28.68	70.51	0.0583

Table LI.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	15.21	30.39	0.0399
50	19.85	41.12	0.0428
100	21.34	44.72	0.0438
200	24.02	51.70	0.0461
400	25.67	54.45	0.0448
800	27.74	59.56	0.0459
1600	29.61	63.87	0.0463

Table LII.—Conductivity of Cobalt Chloride in Ethyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	6.06	7.64	0.0104
50	10.59	13.75	0.0119
100	12.79	17.33	0.0142
200	15.43	20.93	0.0142
400	17.66	24.18	0.0148
800	20.70	28.45	0.0150
1600	23.99	33.59	0.0160

Table LIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	86.42	30.53	18.17	15.21	6.06
50	104.31	33.74	21.55	19.85	10.59
100	109.27	34.64	22.46	21.34	12.79
200	113.73	35.64	23.83	24.02	15.43
400	115.87	37.63	24.76	25.67	17.66
800	116.71	41.89	26.46	27.74	20.70
1600	117.40	42.42	28.68	29.61	23.99

Table LIV.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 25°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	156.36	73.68	44.75	30.39	7.64
50	189.27	85.65	55.21	41.12	13.75
100	197.41	87.60	57.41	44.72	17.33
200	213.40	94.42	63.42	51.70	20.93
400	219.63	97.64	64.00	54.45	24.18
800	220.40	101.33	69.34	59.56	28.45
1600	221.50	103.86	70.51	63.87	33.59

Table LV.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water from 0° to 25° .

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0324	0.0565	0.0585	0.0399	0.0104
50	0.0326	0.0615	0.0625	0.0428	0.0119
100	0.0322	0.0611	0.0622	0.0438	0.0142
200	0.0350	0.0660	0.0664	0.0461	0.0142
400	0.0358	0.0638	0.0634	0.0448	0.0148
800	0.0354	0.0568	0.0648	0.0459	0.0150
1600	0.0355	0.0579	0.0583	0.0463	0.0160

Tables XLIX. to LV. (Figs. XV. and XVI.) for cobalt chloride, in mixtures of ethyl alcohol and water, show a point

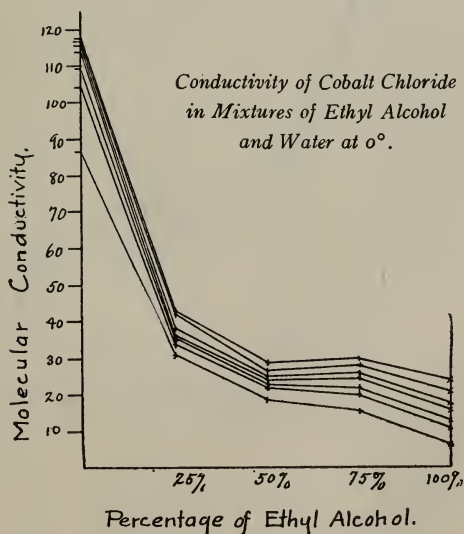


Fig. XV.

of inflection. At 0° the inflection of the curves exists at all dilutions, while at 25° the inflection is marked only at the high

dilutions. Jones and Bingham obtained curves showing points of inflection while working with calcium nitrate, in mixtures of acetone and water.

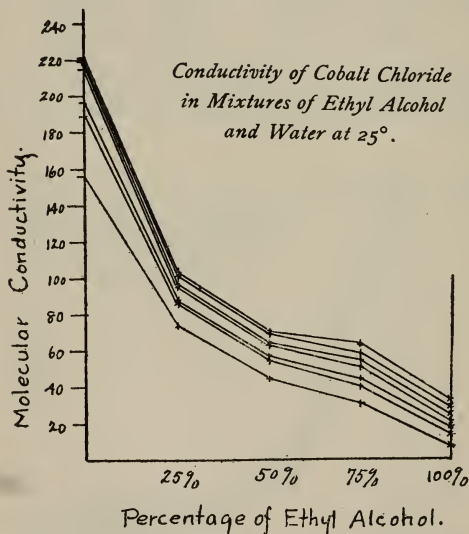


Fig. XVI.

In the pure ethyl alcohol, the temperature coefficients increase with the dilution. They are largest, for the most part, in the 50 per cent mixture.

Table LVI.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	8.82	10.76	0.00880
50	14.66	17.61	0.00805
100	17.32	21.75	0.01022
200	20.23	26.58	0.01255
400	23.75	30.08	0.01070
800	28.34	35.23	0.00972
1600	32.23	41.14	0.01106

Table LVII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	12.89	16.89	0.0124
50	21.46	27.38	0.0110
100	24.31	30.39	0.0100
200	28.63	35.89	0.0101
400	32.28	41.80	0.0118
800	39.21	48.22	0.0092
1600	46.28	58.73	0.0108

Table LVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	22.49	25.53	0.00541
50	35.33	44.31	0.01020
100	40.79	49.90	0.00893
200	48.55	60.62	0.00994
400	54.78	69.42	0.01070
800	63.06	81.13	0.01150
1600	69.29	95.07	0.01490

Table LIX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	6.06	8.82	12.89	22.49	33.46
50	10.59	14.66	21.46	35.33	51.76
100	12.79	17.32	24.31	40.79	60.89
200	15.43	20.23	28.63	48.55	70.45
400	17.66	23.75	32.28	54.78	75.64
800	20.70	28.34	39.21	63.06	86.57
1600	23.99	32.23	46.28	69.29	95.54

Table LX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	7.64	10.76	16.89	25.53	41.78
50	13.75	17.61	27.38	44.31	65.22
100	17.33	21.75	30.39	49.90	76.08
200	20.93	26.58	35.89	60.62	87.37
400	24.18	30.08	41.80	69.42	99.96
800	28.45	35.23	48.22	81.13	117.18
1600	33.59	41.14	58.73	95.07	133.33

Table LXI.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0104	0.00880	0.0124	0.00541	0.00995
50	0.0119	0.00805	0.0110	0.01020	0.01040
100	0.0142	0.01023	0.0100	0.00893	0.00998
200	0.0142	0.01255	0.0101	0.00994	0.00961
400	0.0148	0.01070	0.0118	0.01070	0.01280
800	0.0150	0.00972	0.0092	0.01150	0.01410
1600	0.0160	0.01106	0.0108	0.01490	0.01580

Tables LVI. to LXI. (Figs. XVII. and XVIII.) make it clear that in a mixture of methyl and ethyl alcohols the con-

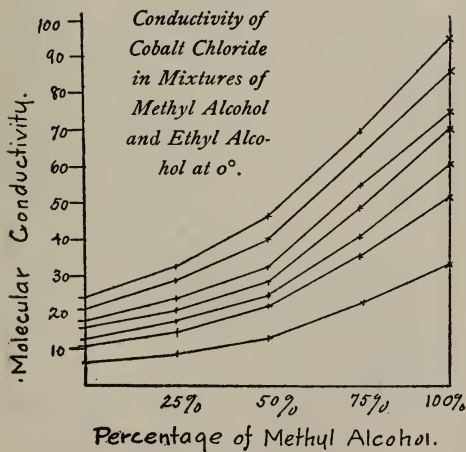


Fig. XVII.

ductivity of cobalt chloride exhibits no minimum value. There is a sagging of the curves, which shows that the values ob-

tained are less than what we should expect from the law of averages.

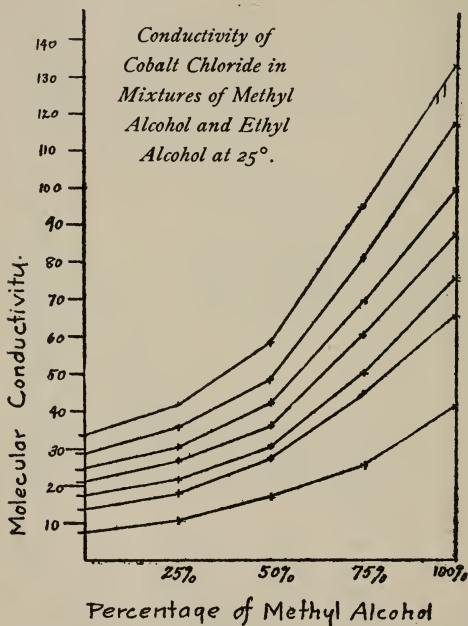


Fig. XVIII.

Table LXII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	64.40	115.38	0.0316
200	67.88	118.42	0.0298
400	69.13	122.39	0.0308
800	72.93	126.88	0.0296
1600	79.34	134.69	0.0279

Table LXIII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	54.42	96.89	0.0312
200	57.79	106.88	0.0340
400	60.29	112.70	0.0348
800	64.54	117.97	0.0331
1600	67.80	125.54	0.0341

Table LXIV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	33.14	70.57	0.0452
200	37.98	84.48	0.0490
400	53.41	94.84	0.0310
800	61.16	109.76	0.0318
1600	68.51	124.95	0.0329

Table LXV.—Conductivity of Cobalt Chloride in Acetone at 0° and 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	10.18	9.47	—0.00279
200	10.96	9.70	—0.00460
400	11.63	9.94	—0.00581
800	12.66	10.11	—0.00806
1600	12.79	10.45	—0.00732

Table LXVI.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Water at 0°.

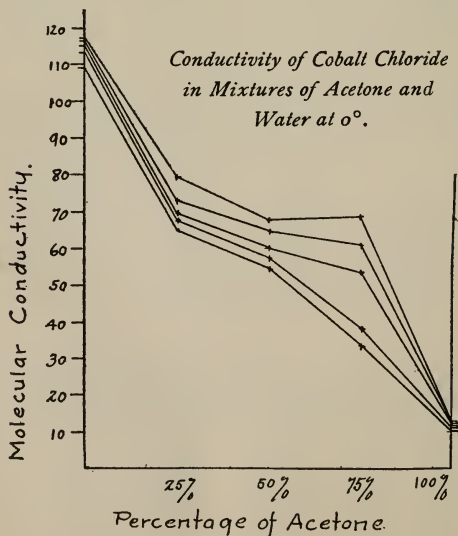
<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	109.27	64.40	54.42	33.14	10.18
200	113.73	67.88	57.79	37.98	10.96
400	115.87	69.13	60.29	53.41	11.63
800	116.71	72.93	64.54	61.16	12.66
1600	117.40	79.34	67.80	68.51	12.79

Table LXVII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	197.41	115.38	96.89	70.57	9.47
200	213.40	118.42	106.88	84.48	9.70
400	219.63	122.39	112.70	94.84	9.94
800	220.04	126.88	117.97	109.76	10.11
1600	221.50	134.69	125.54	124.95	10.45

Table LXVIII.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.0322	0.0316	0.0312	0.0452	—0.00279
200	0.0350	0.0298	0.0340	0.0490	—0.00460
400	0.0358	0.0308	0.0348	0.0310	—0.00581
800	0.0354	0.0296	0.0331	0.0318	—0.00806
1600	0.0355	0.0279	0.0341	0.0329	—0.00732



Tables LXII. to LXVIII. (Figs. XIX. and XX.) for cobalt chloride, in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. Attention should be called to the fact that the *conductivity values in pure*

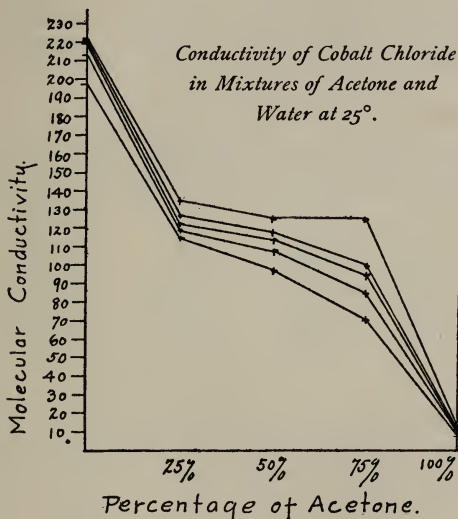


Fig. XX.

acetone, at 25°, are less than the corresponding values at 0°, thus giving negative temperature coefficients. The values in pure acetone for μ_v are small at both temperatures and at all dilutions.

Table LXIX.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	48.10	56.28	0.00680
200	57.33	64.87	0.00526
400	64.43	73.04	0.00534
800	74.60	84.46	0.00529
1600	91.57	100.09	0.00372

Table LXX.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	35.31	39.20	0.00441
200	42.12	46.94	0.00458
400	49.39	55.47	0.00492
800	56.97	66.85	0.00694
1600	67.55	74.11	0.00388

Table LXXI.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v .	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	23.85	24.83	+0.00164
200	28.72	28.67	—0.00007
400	32.74	31.85	—0.00108
800	42.05	38.69	—0.00319
1600	50.94	47.20	—0.00294

Table LXXII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol at 0°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	60.89	48.10	35.31	23.85	10.18
200	70.45	57.33	42.12	28.72	10.96
400	75.64	64.43	49.39	32.74	11.63
800	86.57	74.60	56.97	42.05	12.66
1600	95.54	91.57	67.55	50.94	12.79

Table LXXIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol at 25°.

v .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	76.08	56.28	39.20	24.83	9.47
200	87.37	64.87	46.94	28.67	9.70
400	99.96	73.04	55.47	31.85	9.94
800	117.18	84.46	66.85	38.69	10.11
1600	133.33	100.09	74.11	47.20	10.45

Table LXXIV.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol from 0° to 25° .

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.00998	0.00680	0.00441	+0.00164	—0.00279
200	0.00961	0.00526	0.00458	—0.00007	—0.00460
400	0.01280	0.00534	0.00492	—0.00108	—0.00581
800	0.01410	0.00529	0.00694	—0.00319	—0.00806
1600	0.01580	0.00372	0.00388	—0.00294	—0.00732

From a study of Tables LXIX. to LXXIV. (Figs. XXI. and XXII.), we see that cobalt chloride, in mixtures of acetone and methyl alcohol, gives neither a minimum nor a maximum

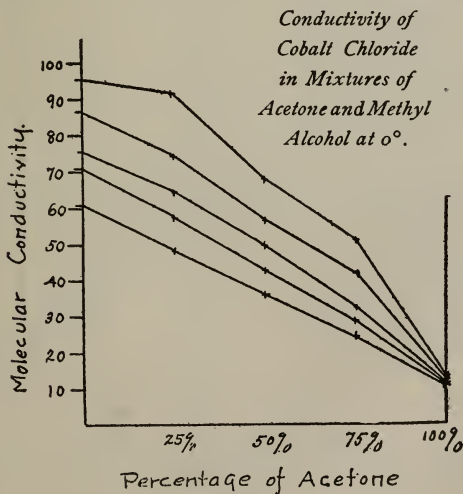


Fig. XXI.

in conductivity. The values at most of the dilutions, are what we should expect from the law of averages. It should be recalled that lithium bromide, in mixtures of acetone and

methyl alcohol, gives a maximum in conductivity at both temperatures.

By studying the temperature coefficients we see that we have to deal with a peculiar phenomenon. In the pure acetone, as already stated, we have *negative temperature coefficients*. In

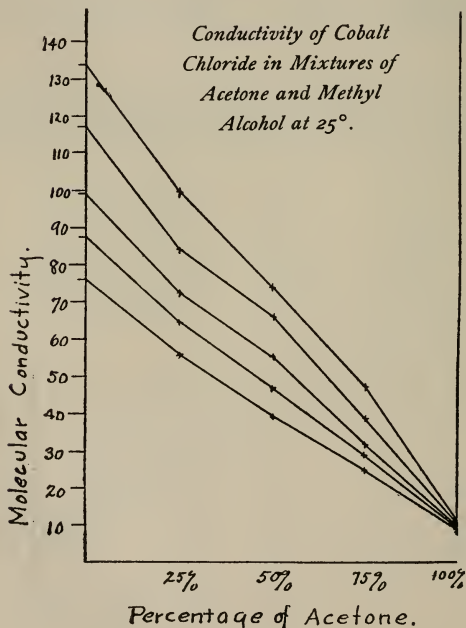


Fig. XXII.

the 75 per cent mixture of acetone and methyl alcohol, beginning with $v = 400$, we again have *negative temperature coefficients*. For $v = 100$ we have the temperature coefficient *positive*, while at $v = 200$ we have practically *no temperature coefficient of conductivity*.

Table LXXV.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
100	14.40	15.43	0.00286
200	18.05	19.47	0.00314
400	21.19	23.67	0.00562
800	26.10	30.20	0.00628
1600	31.80	36.41	0.00580

Table LXXVI.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
100	12.78	12.41	—0.00116
200	15.20	13.91	—0.00339
400	17.95	15.78	—0.00483
800	22.47	18.76	—0.00660
1600	28.67	23.47	—0.00726

Table LXXVII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μv 0°.	μv 25°.	Temperature coefficients.
100	13.46	11.95	—0.00449
200	14.41	12.49	—0.00533
400	14.69	12.69	—0.00544
800	15.74	13.48	—0.00574
1600	17.28	14.19	—0.00715

Table LXXVIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol at 0°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	12.79	14.40	12.78	13.46	10.18
200	15.43	18.05	15.20	14.41	10.96
400	17.66	21.19	17.95	14.69	11.63
800	20.70	26.10	22.47	15.74	12.66
1600	23.99	31.80	28.67	17.28	12.79

Table LXXIX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	17.33	15.43	12.41	11.95	9.47
200	20.93	19.47	13.91	12.49	9.70
400	24.18	23.67	15.78	12.69	9.94
800	28.45	30.20	18.76	13.48	10.11
1600	33.59	36.41	23.47	14.19	10.45

Table LXXX.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.0142	0.00286	—0.00116	—0.00449	—0.00279
200	0.0142	0.00314	—0.00339	—0.00533	—0.00460
400	0.0148	0.00562	—0.00483	—0.00544	—0.00581
800	0.0150	0.00628	—0.00660	—0.00574	—0.00806
1600	0.0160	0.00580	—0.00726	—0.00715	—0.00732

Tables LXXV. to LXXX. (Figs. XXIII. and XXIV.) for

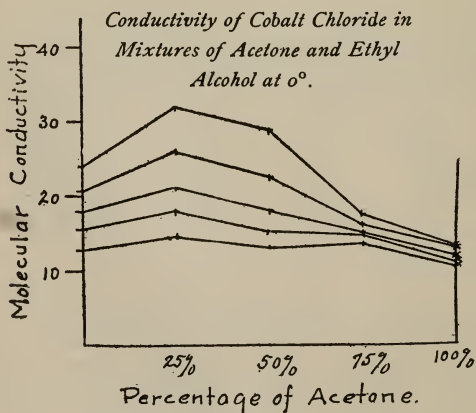


Fig. XXIII.

cobalt chloride, in mixtures of acetone and ethyl alcohol, give

a maximum in conductivity in the 25 per cent mixture, especially at high dilutions.

In the mixtures of acetone and ethyl alcohol we have *negative temperature coefficients* not only in the pure acetone and 75 per cent mixture, but also in the 50 per cent mixture. In

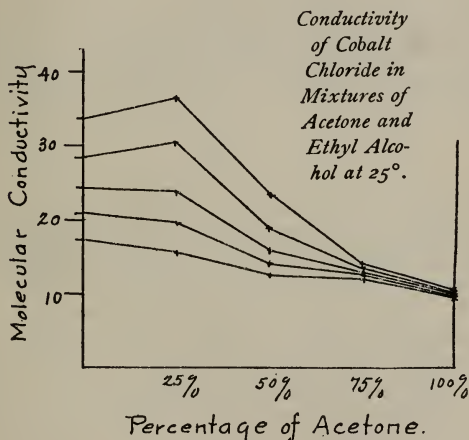


Fig. XXIV.

the case of acetone and methyl alcohol, the temperature coefficients were *negative* only in the pure acetone and 75 per cent mixture. With increase of dilution we have an increase in value of the temperature coefficients, not only in the pure solvents but also in the mixtures.

Viscosity Measurements.

It can be shown that the rate, $\frac{dx}{dt}$, at which the angular dis-

tortion of a portion of fluid changes, is proportional to the shearing stress upon the portion of the fluid. This ratio, shearing stress (S) divided by $\frac{dx}{dt}$, for a given fluid, is called its coefficient of viscosity. It may be written thus,

$$\eta = \frac{S}{\frac{dx}{dt}},$$

in which η is the coefficient of viscosity.

The viscosity of fluids is often determined by the method of Poisseule and of Hagenbach. The viscosity is calculated by the formula¹

$$\mu = \frac{P\pi r^4 t}{8 v l},$$

where P is the actual pressure, diminished by that pressure which would be necessary to give to the fluid, while flowing through capillary tubes, the kinetic energy possessed by it; t is the time of flow through the capillary tube of radius r and length l ; v is the volume of fluid flowing in time t .

The viscosity of fluids is, however, most commonly found by the method recommended by Ostwald.² We find by this method the time of flow of a fixed volume through a capillary tube, under the pressure due to the difference in level of the free surfaces of the fluid. The viscosity is found from the ratio of the time of flow for the fluid in question to the time of flow for an equal volume of water, multiplied by the specific gravity of the solution. This is expressed by the formula

$$\eta = \eta_0 \frac{S t}{S_0 t_0},$$

in which η_0 is the coefficient of viscosity for water, S_0 its specific gravity, and t_0 its time of flow, at a given temperature. The specific gravity and time of flow of the liquid in question are given by S and t , respectively.

In the following tables containing viscosity data, the values

¹ Hagenbach: Pogg. Ann., 19, 385 (1860).

² Ostwald-Luther: Physiko-Chemische Messungen, Zweite Aufl., p. 259.

for pure water, at 0° and 25° , taken from the work of Thorpe and Rodger,¹ are used, and all the other values are referred to them; η is the viscosity, while ϕ , which represents fluidity, is obtained from the expression

$$\phi = \frac{1}{\eta}.$$

The density of the liquid in question, at 0° and 25° , was compared with the density of water at 0° and 25° , respectively. The density of water at 0° and 25° was taken from data given in Landolt and Börnstein's tables.

The values of η and ϕ for the solvents methyl alcohol, ethyl alcohol, acetone and mixtures of these are taken from the work of Jones and Bingham.²

Table LXXXI.—Fluidity of Water at 0° and 25° .

<i>v.</i>	$\mu\ 0^{\circ}$.	$\phi\ 0^{\circ}$.	$\mu\ 25^{\circ}$.	$\phi\ 25^{\circ}$.	Temperature coefficient.
Solvent	0.01778	56.24	0.00891	112.3	0.0398

Table LXXXII.—Fluidity of Lithium Bromide in Water at 0° and 25° .

<i>v.</i>	$\mu\ 0^{\circ}$.	$\phi\ 0^{\circ}$.	$\eta\ 25^{\circ}$.	$\phi\ 25^{\circ}$.	Temperature coefficients.
10	0.01874	53.36	0.009077	110.17	0.0425
1600	0.01827	54.73	0.008963	111.57	0.0415
Solvent	0.01778	56.24	0.008910	112.30	0.0398

Table LXXXIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25° .

<i>v.</i>	$\eta\ 0^{\circ}$.	$\phi\ 0^{\circ}$.	$\eta\ 25^{\circ}$.	$\phi\ 25^{\circ}$.	Temperature coefficients.
10	0.034216	29.22	0.01440	69.43	0.0550
1600			0.01420	70.42	
Solvent	0.03335	29.98	0.01409	70.94	0.0546

¹ Phil. Trans., 185A, 307 (1894).

² THIS JOURNAL, 34, 481 (1905).

Table LXXXIV.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.03703	27.00	0.01680	59.53	0.0482
1600			0.01639	61.01	
Solvent	0.03642	27.46	0.01611	62.04	0.0503

Table LXXXV.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10			0.01345	74.32	
1600			0.01298	77.00	
Solvent	0.02576	38.82	0.01283	77.92	0.0402

Table LXXXVI.—Fluidity of Lithium Bromide in Methyl Alcohol at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.008994	111.18	0.006124	163.28	0.0187
1600	0.008346	119.82	0.005635	177.46	0.0192
Solvent	0.008185	122.20	0.005659	176.70	0.0178

Table LXXXVII.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 0° and 25°.

Fluidities at 0°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36	29.22	27.00		111.18
1600	54.73				119.82
Solvent	56.24	29.98	27.46	38.82	122.20

Fluidities at 25°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	110.17	69.43	59.53	74.32	163.28
1600	111.57	70.42	61.01	77.00	177.46
Solvent	112.30	70.94	62.04	77.92	176.70

Table LXXXVIII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Methyl Alcohol and Water from 0° to 25°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425	0.0550	0.0482		0.0187
1600	0.0415				0.0192
Solvent	0.0398	0.0546	0.0503	0.0402	0.0178

Table LXXXIX.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10			0.01832	54.57	
1600			0.01818	55.00	
Solvent	0.05264	18.99	0.01810	55.22	0.0763

Table XC.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.06922	14.45	0.02453	40.77	0.0728
1600			0.02407	41.53	
Solvent	0.06720	14.88	0.02405	41.56	0.0717

Table XCI.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.02204	45.36	
1600			0.02139	46.75	
Solvent	0.05167	19.35	0.02118	47.21	0.0575

Table XCII.—Fluidity of Lithium Bromide in Ethyl Alcohol at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.02441	40.96	0.01366	73.18	0.0314
1600	0.02199	45.48	0.01224	81.69	0.0318
Solvent	0.01856	53.88	0.01106	90.35	0.0271

Table XCIII.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36		14.45		40.96
1600	54.73				45.48
Solvent	56.24	18.99	14.88	19.35	53.88

Fluidities at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	110.17	54.57	40.77	45.36	73.18
1600	111.57	55.00	41.53	46.75	81.69
Solvent	112.30	55.22	41.56	47.21	90.35

Table XCIV.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Ethyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425		0.0728		0.0314
1600	0.0415				0.0318
Solvent	0.0398	0.0763	0.0717	0.0575	0.0271

Tables LXXXI. to XCIV. (Fig. XXV.) show that there is a minimum of fluidity not only in the case of the mixtures of the pure solvents—methyl alcohol and water, and ethyl alcohol and water—at both temperatures, but also in the case of lithium bromide dissolved in the above solvents. The fluidity of a liquid being the reciprocal of its viscosity, the viscosity curve would pass through a maximum in the above cases. A large number of investigations have been carried out on the viscosities of the alcohols and water, notably, by Poisseuille,¹ Stephan,² Pagliani and Battelli,³ Noack,⁴ and Traube.⁵ Quite recently some work has been done on the viscosity of mixtures

¹ Mem. Inst. Paris, 9, 433 (1896).

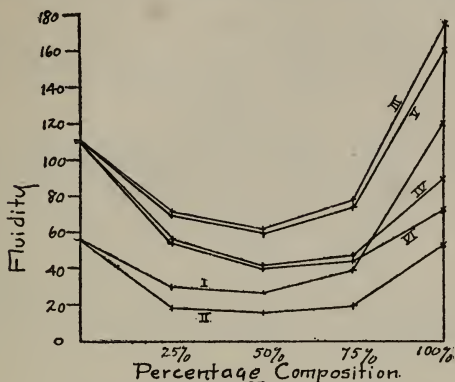
² Wied. Ann., 17, 673 (1883).

³ Atti. di R. Ac. delle Sc. d. Torino, 20, 607 (1885).

⁴ Wied. Ann., 27, 289 (1886).

⁵ Ber. d. chem. Ges., 19, 871 (1886).

of the alcohols and water by Dunstan,¹ Blanchard,² and Varenne and Godefroy.³ All of these workers have found that, in the



- I. Methyl Alcohol and Water at 0°.
- II. Ethyl Alcohol and Water at 0°.
- III. Methyl Alcohol and Water at 25°.
- IV. Ethyl Alcohol and Water at 25°.
- V. 0.1 N LiBr in CH₃OH and H₂O at 25°.
- VI. 0.1 N LiBr in C₂H₅OH and H₂O at 25°.

Fig. XXV.

case of mixtures of the alcohols and water, the viscosity of the mixture is much greater than would be expected from the law of averages.

Jones and Carroll⁴ have calculated the various fluidities of mixtures of methyl and ethyl alcohol and water, for the temperatures 0°, 10°, 20° and 30°, from the results of Pagliani and Battelli⁴ and of Traube⁴ and have plotted the fluidity curves. Their curves were similar to those which we obtained.

¹ J. Chem. Soc., 85, 817 (1904).

² J. Am. Chem. Soc., 26, 1315 (1904).

³ Compt. rend., 137, 992 (1903); 138, 990 (1904).

⁴ Loc. cit.

Table XCV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Methyl Alcohol and Water.

		Fluidity.				
v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0398	0.0546	0.0503	0.0402	0.0178
		Conductivity.				
10	LiBr	0.0329	0.0435	0.0410	0.0314	0.01590
1600	LiBr	0.0357	0.0437	0.0420	0.0335	0.01810
10	CoCl ₂	0.0324	0.0440	0.0400	0.0324	0.00995
1600	CoCl ₂	0.0355	0.0472	0.0411	0.0257	0.01580

Table XCVI.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Ethyl Alcohol and Water.

		Fluidity.				
v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0398	0.0763	0.0717	0.0575	0.0271
		Conductivity.				
10	LiBr	0.0329	0.0557	0.0595	0.0437	0.0253
1600	LiBr	0.0357	0.0448	0.0596	0.0465	0.0242
10	CoCl ₂	0.0324	0.0565	0.0585	0.0399	0.0104
1600	CoCl ₂	0.0355	0.0579	0.0583	0.0463	0.0160

Tables XCV. and XCVI. show that the temperature coefficients of fluidity and conductivity vary in the same manner. The latter are, however, uniformly smaller than the former.

Table XCVII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.01366	73.19	
1600			0.01356	73.72	
Solvent	0.0293	34.12	0.01276	78.37	0.0518

Table XCVIII.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.03102	32.23	0.01428	70.00	0.0468
1600			0.01369	73.00	
Solvent	0.03027	33.03	0.01330	74.96	0.0508

Table XCIX.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.009562	104.58	
1600			0.009263	107.95	
Solvent	0.017	58.8	0.008904	112.30	0.0364

Table C.—Fluidity of Lithium Bromide in Acetone at 0° and 25°.

<i>v.</i>	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.004302	232.45	0.003484	286.96	0.0093
1600	0.004117	242.85	0.003339	299.42	0.0093
Solvent	0.004097	244.10	0.003237	308.90	0.0106

Table CI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Water at 0° and 25°.

Fluidities at 0°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36		32.23		232.45
1600	54.73				242.85
Solvent	56.24	34.12	33.03	58.80	244.10

Fluidities at 25°.

<i>v.</i>	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	110.17	73.19	70.00	104.58	286.96
1600	111.57	73.72	73.00	107.95	299.42
Solvent	112.30	78.37	74.96	112.30	308.90

Table CII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Water from 0° to 25° .

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425		0.0468		0.0093
1600	0.0415				0.0093
Solvent	0.0398	0.0518	0.0508	0.0364	0.0106

Table CIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25° .

v.	μ 0° .	ϕ 0° .	μ 25° .	ϕ 25° .	Temperature coefficients.
10			0.005455	183.30	
1600			0.005068	197.29	
Solvent	0.006498	153.90	0.004615	216.70	0.0163

Table CIV.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25° .

v.	μ 0° .	ϕ 0° .	μ 25° .	ϕ 25° .	Temperature coefficients.
10	0.006265	159.6(?)	0.004527	220.87	0.0153
1600	0.005774	173.17	0.004234	236.18	0.0145
Solvent	0.005336	187.40	0.003891	257.10	0.0148

Table CV.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25° .

v.	μ 0° .	ϕ 0° .	μ 25° .	ϕ 25° .	Temperature coefficients.
10			0.003775	264.88	
1600			0.003581	279.25	
Solvent	0.004501	222.20	0.003446	290.10	0.0122

Table CVI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 0° and 25° .

Fluidities at 0° .

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	111.18		159.6(?)		232.45
1600	119.82		173.17		242.85
Solvent	122.20	153.90	187.40	222.20	244.10

Fluidities at 25° .

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	163.28	183.30	220.87	264.88	286.96
6100	177.46	197.29	236.18	279.25	299.42
Solvent	176.70	216.70	257.00	290.10	308.90

Table CVII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0187		0.0153		0.0093
1600	0.0192		0.0145		0.0093
Solvent	0.0178	0.0163	0.0148	0.0122	0.0106

Table CVIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.008218	121.69	
1600			0.007731	129.34	
Solvent	0.01041	96.08	0.006714	148.90	0.022

Table CIX.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.007353	136.0	0.005554	180.05	0.0129
1600			0.005165	193.59	
Solvent	0.006801	147.0	0.004874	205.20	0.0148

Table CX.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.004237	235.99	
1600			0.003874	258.10	
Solvent	0.00499	200.4	0.003776	264.80	0.01296

Table CXI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	40.96		136.00		232.45
1600	45.48				242.85
Solvent	53.88	96.08	147.00	200.40	244.10

Fluidities at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	73.18	121.69	180.05	235.99	286.96
1600	81.69	129.34	193.59	258.10	299.42
Solvent	90.35	148.90	205.20	264.80	308.90

Table CXII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25° .

ν .	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0314		0.0129		0.0093
1600	0.0318				0.0093
Solvent	0.0271	0.022	0.0148	0.01296	0.0106

Tables XCVII. to CXII. (Figs. XXVI., XXVII. and XXVIII.) show that there is a minimum of fluidity for the

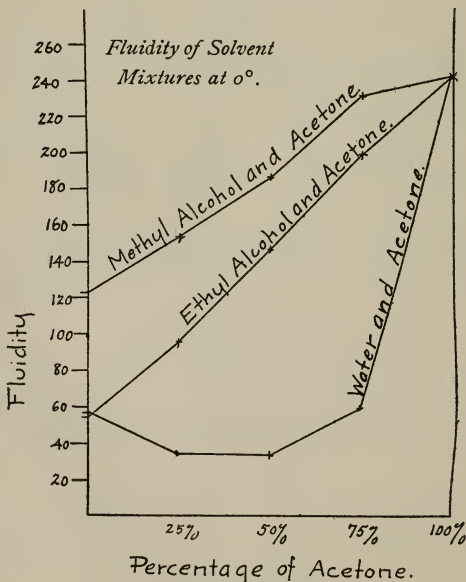


Fig. XXVI.

solvents only in the case of acetone and water. This fact was

pointed out by Jones and Bingham. Lithium bromide, in a mixture of acetone and water, shows a similar minimum. Jones and Bingham also found that in the mixtures of acetone with methyl alcohol, somewhat larger values were obtained than would be expected from the fluidities of the pure solvents.

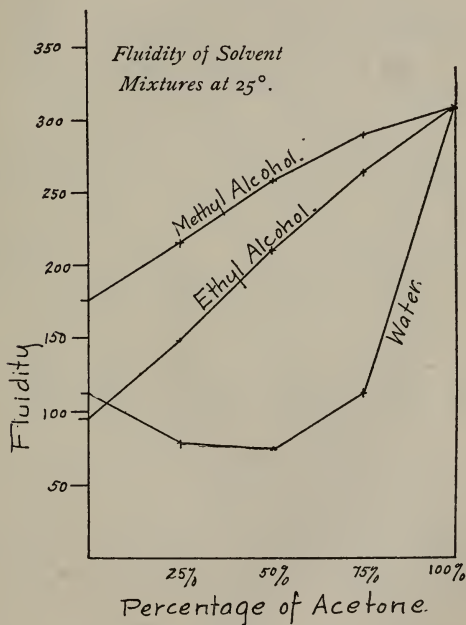


Fig. XXVII.

This effect is not quite so apparent in the case of acetone and ethyl alcohol. We obtained similar results in the case of lithium bromide in these solvents. It is to be especially noticed

that the viscosity curves in all cases, for mixtures of acetone with the alcohols, show a marked sagging.

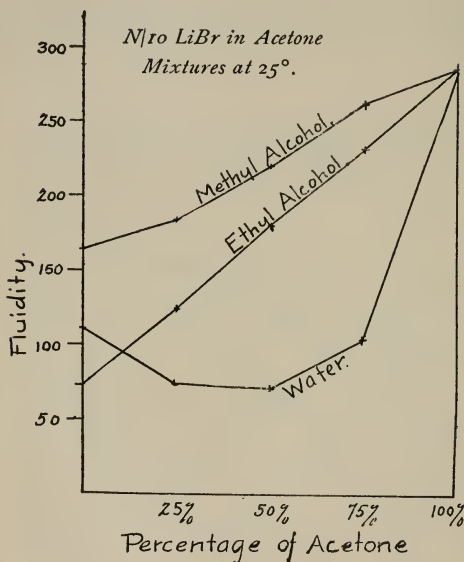


Fig. XXVIII.

Table CXIII.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Water.

		Fluidity.				
v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0398	0.0518	0.0508	0.0364	0.0106
Conductivity.						
10	LiBr	0.0329	0.0429	0.0432	0.0315	0.00729
1600	LiBr	0.0357	9.0401	0.0437	0.0372	0.00847
100	CoCl ₂	0.0322	0.0316	0.0312	0.0452	—0.00279
1600	CoCl ₂	0.0355	0.0279	0.0341	0.0329	—0.00732

Table CXIV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Methyl Alcohol.

<i>Fluidity.</i>						
<i>v.</i>	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0178	0.0163	0.0148	0.0122	0.0106

<i>Conductivity.</i>						
10	LiBr	0.0159	0.0143	0.00939	0.0112	0.00729
1600	LiBr	0.0181	0.0153	0.01340	0.0104	0.00847
100	CoCl ₂	0.00998	0.0068	0.00441	0.00164	—0.00279
1600	CoCl ₂	0.0158	0.00372	0.00388	—0.00294	—0.00732

Table CXV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Ethyl Alcohol.

<i>Fluidity.</i>						
<i>v.</i>	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0271	0.022	0.0148	0.0129	0.0106

<i>Conductivity.</i>						
10	LiBr	0.0253	0.0168	0.0135	0.0085	0.00729
1600	LiBr	0.0242	0.0206	0.0159	0.0103	0.00847
100	CoCl ₂	0.0142	0.00286	—0.00116	—0.00449	—0.00279
1600	CoCl ₂	0.0160	0.00580	—0.00726	—0.00715	—0.00732

Tables CXIII. to CXV. show that the temperature coefficients of fluidity and conductivity, in the case of lithium bromide, vary in the same manner, although the latter are, for the most part, smaller than the former. Abnormal results were obtained with cobalt chloride in mixtures of acetone with the alcohols, in so far as the temperature coefficients of conductivity are concerned.

PART III.

DISCUSSION OF RESULTS.

A. Fluidity and Conductivity.

That there is a parallelism between conductivity and fluidity has been previously pointed out in the introduction to this

paper ; and since the conductivity of a solution is dependent, in part, upon its fluidity, we shall first discuss the fluidity curves and then, in connection with them, the conductivity curves.

When methyl alcohol, ethyl alcohol, or acetone is mixed with water there is a contraction in volume and an evolution of heat, and we have a large deviation of the fluidity curve from a straight line. In other words, we have a marked viscosity maximum—a fact which seems to be more or less general whenever water and organic solvents are mixed. In addition to methyl and ethyl alcohols and acetone, propyl and isopropyl alcohols, propionic acid, butyric and isobutyric acids give, when mixed with water, viscosity maxima. In every case there is a greater decrease in fluidity than would be expected from the law of averages.

When methyl and ethyl alcohol are mixed they do not exhibit the same phenomena as is shown in the case of mixtures of organic solvents with water. Arrhenius¹ states that there is no observable change when these alcohols are brought together.

When acetone is mixed with methyl or ethyl alcohol, the fluidity curve of the mixture is approximately a straight line. The same is true when we have an electrolyte dissolved in mixtures of these solvents.

From a consideration of the fluidity curves and conductivity curves for lithium bromide in mixtures of methyl alcohol and water, it is quite evident that the minimum of fluidity corresponds to the minimum of conductivity, both generally occurring in the 50 per cent mixtures of the solvents. The drop in fluidity is more pronounced at the lower temperature, and, similarly, the drop in conductivity. In fact, at the higher temperature, the minimum of conductivity occurs in the 75 per cent mixture until $v = 100$, where there is a shifting of the minimum to the 50 per cent mixture.

In the case of mixtures of ethyl alcohol and water, the minimum of fluidity is in the 50 per cent mixture, and more marked at the lower temperature. The conductivity minimum in this case occurs in the 75 per cent mixture, and is very

¹ *Z. physik. Chem.*, 1, 285 (1887).

slight indeed at 25°, although the values, in each case, are much less than we should expect from the law of averages. Thus we have, in both the case of methyl alcohol and water, and of ethyl alcohol and water, a tendency for the shifting of the minimum towards the mixture containing the greater per cent of alcohol, whenever we have a rise in temperature.

Stephan,¹ working with mixtures of ethyl alcohol and water, found that the temperature coefficients of conductivity and of fluidity were very similar. A minimum in his curves was observed, and he proposed the relations

$$k = \frac{K H}{\eta} \quad \text{and} \quad k = \frac{w K H}{w' \eta},$$

the first holding for the mixtures up to the minimum point, and the second from that point on. K is the same in both formulæ, and is the conductivity of the equivalent aqueous solution of the electrolyte; k is the conductivity in the mixture; H and η are the viscosity coefficients for water and for the mixture, respectively. w and w' are the per cents of water in the mixture and in the aqueous alcoholic mixtures of minimal fluidity, respectively. Stephan concluded that each ion carries with it molecules of the solvent, and that the ionic friction consists in friction between these molecules and the rest of the solvent. Thus we have very early the idea of ionic hydration introduced.

This idea of ionic hydration, or ionic spheres, was further extended by Kohlrausch,² who proposed the hypothesis that "about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion The electrolytic resistance is a frictional one that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portions of the solvent diminishes as the atmosphere becomes of greater dimensions. For a slow moving ion there would be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, providing the atmosphere

¹ Wied. Ann., 17, 673 (1883).

² P. Roy. Acad., 71, 338 (1903).

does not change its dimensions with temperature. However, if the atmosphere becomes smaller with rise in temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. This seems to be true for the slowest moving, univalent ion, Li."

In the case of the alcohols and water, this minimum of conductivity is entirely accounted for by some investigators on the basis of the formation of hydrates. This view was suggested by Zelinsky and Krapivin.¹ The minimum in fluidity is attributed to the formation of molecular aggregations, which are formed by mixing the solvents. In the case of methyl alcohol and acetone, or ethyl alcohol and acetone, since the fluidity curve is a straight line, we conclude that the molecular aggregations of these solvents are not changed in size when the solvents are mixed. This is what we should expect if the fluidities are additive, a fact which has been shown recently by Bingham² to be true. From the above, we see that the conductivity minimum is generally accompanied by a fluidity minimum, and that both minima are more marked at the lower temperatures. Also, that an increase in temperature tends to shift the minimum towards the mixture containing a greater per cent of alcohol or acetone, as the case may be. Thus, we believe that *a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum of conductivity.* In the case when the conductivity minimum is in the 75 per cent mixture, while the minimum of fluidity is in the 50 per cent mixture, as it is with ethyl alcohol and water, we believe that the explanation is to be found in the fact that the ethyl alcohol and water mixtures have a much greater viscosity than those of methyl alcohol and water. When the minimum shifts with an increase in dilution, there may be an increase in dissociation.

However, we do not believe that the above explanation accounts entirely for the conductivity minimum. Since conductivity is dependent upon the number and velocity of the ions,

¹ Z. physik. Chem., **21**, 35 (1896).

² THIS JOURNAL, **35**, 195 (1906).

there is no doubt but that an increase in viscosity retards the velocity of the ions, but we think that *the change in the size of the ionic sphere, or the atmosphere which surrounds the ion*, should be taken into account. The movement of the ion depends not only upon its composition, but also upon its attraction for the surrounding solvent, which causes an atmosphere of the solvent to be formed about the ion. Lithium is an extremely slow moving ion, or, in other words, one with a very large ionic sphere. Now the atmosphere becomes larger with decreasing temperature. Thus, we have evidence that the change in dimensions of the ionic spheres must be taken into account in dealing with fluidity and, consequently, with conductivity from the fluidity data of lithium bromide. The fluidity values are, on the whole, small, due to the large atmosphere surrounding the lithium ion. This atmosphere increases with decrease in temperature, and thus produces the smaller fluidity values at the lower temperature.

We should not, however, lose sight of the fact that if viscosity is in any way dependent upon the attractions between the molecules, whenever there is a contraction in mixing two solvents as there is in the case of the alcohols and water, then the molecules will be brought closer together and the attractions will be increased between the molecules. It is obvious from this that we should get a fluidity value different from that calculated from the law of averages.

The statement was made above that fluidities are sometimes additive. That is, the resulting fluidity of a mixture of two solvents is equivalent to the sum of the fluidities of each solvent. Formulated, this would be,

$$(k_1 + k_2)\phi = k_1\phi_1 + k_2\phi_2 \dots \dots (1),$$

where ϕ is the resultant fluidity, ϕ_1 and ϕ_2 the respective fluidities of the components of amounts k_1 and k_2 .

Jones and Bingham¹ have pointed out that this expression is similar to the conception which we have in electricity, where the conductance of several conductors, in parallel, is represented by the sum of their separate conductances. The con-

¹ THIS JOURNAL, 134, 481 (1905).

ductance of a pair of conductors, of different material, is, for a unit length,

$$(\sigma_1 + \sigma_2)C = c_1\sigma_1 + c_2\sigma_2,$$

where σ_1 and σ_2 are the areas of cross section of the conductors, c_1 and c_2 their respective conductances, and C the resulting conductance.

By a simple mathematical deduction, Jones and Bingham have shown that if fluidities are additive, viscosities cannot be additive. They derived the formula

$$K'_1 H = \frac{\eta_1 \eta_2}{\mu_2 - \eta_1} \dots \dots \dots (2),$$

where η_1 and μ_2 are the viscosities of the components and H that of the mixture

$$K'_1 = K_1 + \frac{\eta_1}{\eta_2 - \eta_1},$$

where K_1 has the same significance as in equation 1.

Since $\frac{\eta_1 \eta_2}{\eta_2 - \eta_1}$ is a constant, equation (2) is considered to represent an equilateral hyperbola, the Y-axis of which is at a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin to which equation (1) is referred. Thus, the conclusion is drawn that the *hyperbola is the normal curve for viscosities and not the straight line*. This fact accounts for the sagging of the viscosity curves or, in other words, the viscosities of the mixtures are not proportional directly to the amounts of the components. The above only holds in case we have a mixture of two liquids which are made up of particles that do not interact in any way with each other, as in the case of acetone and ethyl alcohol.

When we have contraction or expansion on mixing two liquids, the hyperbola would not represent the viscosity curve of the mixtures, but we get a curve of the form already described.

By examining the viscosity data of the mixtures of acetone with methyl alcohol and ethyl alcohol, and also the data for lithium bromide in these mixtures, we see that the viscosity of

a mixture is, in most instances, slightly lower than would be expected from the law of averages. In these cases the fluidity curves are straight lines. In the recent work of Bingham¹ this has been shown to be frequently true where organic solvents are mixed.

Let us now consider the maximum in conductivity obtained with lithium bromide in mixtures of acetone with methyl and ethyl alcohols. Cobalt chloride gave a maximum in conductivity only in the case of acetone with ethyl alcohol. In the former case the maximum occurs entirely in the 75 per cent mixture, while in the latter only in the 25 per cent mixture.

This phenomenon had also been observed by Jones and Bingham, working with lithium nitrate and calcium nitrate in mixtures of acetone with the alcohols. As pointed out by them, this must be due either to an increase in dissociation in the 75 per cent mixture, or to the diminution in the size of the ionic spheres.

In discussing the fluidity curves, we pointed out that, when acetone was mixed with the alcohols, we did not obtain complex molecular aggregates. It is, then, impossible for the mixture to be more associated than the pure solvents, and we, therefore, cannot have an increase in dissociation if the hypothesis of Dutoit and Aston is true.

From an examination of the conductivity tables of lithium bromide we see that we have by no means reached the limiting conductivity values in the pure acetone, or the 75 per cent mixtures of acetone with the alcohols. It is nearly reached only with the pure alcohols. Thus, we could not have complete dissociation in these mixtures. The conductivity maximum should also manifest itself in the case of cobalt chloride, in mixtures of acetone with methyl alcohol, but this is contrary to what we have observed. We, therefore, accept the view, held tentatively by Jones and Bingham, that *the maximum in conductivity is due primarily to a change in the dimensions of the ionic spheres.*

Attention should be called to the fact that cobalt chloride, in mixtures of acetone with water, shows a tendency toward a

¹ *Loc. cit.*

maximum in conductivity in the 75 per cent mixture, notwithstanding the great decrease in fluidity.

Thus we see that the tendency towards a maximum in conductivity, in mixtures of acetone with other solvents, is very marked.

Let us now sum up the cases where maxima in conductivity have been obtained in the acetone mixtures. Jones and Bingham obtained the maximum with lithium nitrate and calcium nitrate, in mixtures of acetone with methyl or ethyl alcohol. Under similar conditions, we have obtained the maximum in the case of lithium bromide in these mixtures. Cobalt chloride gave the maximum only in a mixture of acetone with ethyl alcohol. Jones and Bingham showed that lithium nitrate and calcium nitrate, in mixtures of acetone with water, show a tendency towards a maximum. We have observed the same fact with cobalt chloride in a mixture of acetone with water.

B. Temperature Coefficients.

That conductivity is affected by temperature was observed as early as 1844 by Ohm.¹ In 1875 it was established by Kohlrausch² that the conductivity of aqueous solutions of electrolytes, in general, increases with the temperature and that, for ordinary temperatures, this relation may be represented by the linear equation,

$$\lambda_t = \lambda_0 (1 + \alpha t),$$

where λ represents the molecular conductivity, t the temperature in question, and α is a constant.

Arrhenius,³ in 1889, showed, from theoretical considerations, that the relation between conductivity and temperature is not a linear one, as suggested by Kohlrausch. He established the fact that conductivity at first increases with rise in temperature, reaches a maximum value, and then decreases. He verified this for solutions of hypophosphorous acid and phosphoric acid, the former having a maximum conductivity at about 55° and the latter at 75°.

¹ Pogg. Ann., 63, 403 (1844).

² *Ibid.*, 154, 224 (1875).

³ Z. physik. Chem., 4, 96 (1889).

Since Arrhenius made these measurements, maxima of conductivity have been found for solutions of copper sulphate and for a number of organic acids. The maximum conductivity of most aqueous solutions, however, is at so high a temperature that experimental difficulties have prevented the verification of the above theory of Arrhenius for many electrolytes.

Maxima of conductivity have been found by Miss Maltby,¹ Hagenbach,² Noyes and Coolidge,³ and others, all working at elevated temperatures.

In the case of non-aqueous solvents there is more evidence available for the existence of conductivity-temperature curves, containing maxima.

Franklin and Kraus⁴ found that, at high temperatures, the conductivity of solutions in liquid ammonia decreases with rise in temperature. Miss Maltby⁵ showed that, at atmospheric temperatures, the conductivity of an ethereal solution of hydrochloric acid decreases as the temperature rises. Cattaneo⁶ obtained negative temperature coefficients in ether and alcohol.

Kraus,⁷ in his investigations of solutions in methyl and ethyl alcohols, also found that the conductivity passes through a maximum with rise in temperature.

Jones⁸ explains these maxima in the conductivity curves thus: "The ions move faster and faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less and less with rise in temperature and, consequently, its dissociating power becomes less and less. This, of course, diminishes the conductivity. The maximum in the conductivity curve represents the temperature at which these opposite influences become equal."

In a very recent article, Jones and West⁹ have pointed out the effect of temperature on dissociation, and have worked out

¹ Z. physik. Chem., **18**, 155 (1895).

² Ann. d. Phys., **5**, 276 (1901).

³ Z. physik. Chem., **46**, 323 (1904). J. Am. Chem. Soc., **26**, 134 (1904).

⁴ THIS JOURNAL, **24**, 83 (1900).

⁵ Z. physik. Chem., **18**, 133 (1895).

⁶ Rend. Lincei, [5], **2**, 1, 295 (1893); [5], **2**, 2, 112 (1893).

⁷ Phys. Rev., **18**, 40 (1904).

⁸ THIS JOURNAL, **31**, 584 (1904).

⁹ *Ibid.*, **34**, 357 (1905).

a large number of temperature coefficients of conductivity in aqueous solutions. They employed 32 substances, inorganic and organic, with very different degrees of dissociation. The range of temperature over which their investigation extended was from 0° to 35° . They found that, while conductivity increases with rise in temperature, dissociation decreases with rise in temperature.

Jones¹ has recently pointed out the bearing of hydrates on the temperature coefficients of conductivity of aqueous solutions. Jones and West, in their work, showed that with an increase of temperature there was a decrease in dissociation. Therefore, *the increase in conductivity with rise in temperature is primarily due to an increase in the velocities with which the ions move.* The velocity of the ions is conditioned chiefly by the viscosity of the medium and the size of the ion. At the higher temperature the force which drives the ion is greater, and the fluidity of the medium through which the ion moves would be greater. Both of these factors increase the velocity of the ions and, consequently, increase the conductivity as the temperature is raised. Jones calls attention to the fact that *the mass of the ion decreases with rise in temperature.* He does not refer to the charged atom or group of atoms which are usually termed the ion, but to this charged nucleus plus a larger or smaller number of molecules of water, which are attached to it and which it drags along with it in its motion through the remainder of the solvent.

At the higher temperature the hydrate formed by the ion is less complex than at a lower temperature. The less the number of molecules of water combined with the ion, the smaller the mass of the ion and the less its resistance when moving through the solvent. Therefore, the ion will move faster at the higher temperature and the conductivity of the solution will increase with rise in temperature.

Jones also points out the fact that, at the higher dilution, the temperature coefficient of conductivity for any given substance is greater than at the lower dilutions. The hydrate at the higher dilution is more complex than at the lower. This

¹ THIS JOURNAL, 35, 445 (1906).

being so, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

After this brief review of the most important facts which have been found concerning the effect of temperature on conductivity, let us study the temperature coefficients which we obtained.

In a previous paper¹ we have pointed out the presence of *solvates* in non-aqueous solutions, not only in the case of lithium bromide but also for several other electrolytes. That there is a combination of the solvent with the dissolved substance to form *solvates* is now a generally accepted fact.

In the pure solvents, with but one exception, the temperature coefficients of conductivity are greater at the higher dilutions than at the lower. This may be explained by the fact that if the solvate at the higher dilution is more complex than at the lower, then the change in the composition of the solvate in question, with change in temperature, is greater at the higher dilution. Consequently, the more dilute the solution the greater the temperature coefficient of conductivity.

In the mixtures of the solvents we found that, in practically every case, there was an increase in the temperature coefficients with an increase in dilution. There is a combination of the solvent and dissolved substance to form a *solvate*, and we believe the explanation is the same as that given above.

This same fact has been found to be true by Jones and his co-workers in many other cases. If we examine the data obtained by Jones and Lindsay in their work, we see that the temperature coefficients of conductivity increase with the dilution for potassium iodide, ammonium bromide, strontium iodide and lithium nitrate, in mixtures of water, methyl and ethyl alcohol and binary mixtures of these solvents. In some few cases the increase, however, is small. Similar results are found by a study of the work of Jones and Carroll, who worked with a number of electrolytes in mixtures of the same

¹ THIS JOURNAL, 35, 316 (1906).

solvents. Jones and Bingham, in their work, observed the fact that in acetone, and in some few acetone mixtures, the temperature coefficients decreased with the dilution. In most cases, however, there was a slight increase with an increase in dilution.

Thus, the fact that at the higher dilutions the temperature coefficients are greater than at the lower, holds, in general, not only for aqueous solutions, as pointed out by Jones, but also for organic solvents and for mixtures of these solvents in most of the cases thus far studied.

We have seen in the historical review that there are a few cases on record where the conductivity decreases with rise in temperature. This has been found to be true, generally, only at high temperatures and after a maximum has been reached. Bousfield and Lowry¹ have shown that we should expect this upper limit of conductivity on account of the decrease in dissociation with rise in temperature. They combine the formula of Slotte² for variation of fluidity,

$$\eta_0/\eta = 1 + \beta t)^n,$$

which holds at low temperatures, with that of Abegg and Seitz for decrease in dielectric constant,

$$D/D' = e^{-at},$$

and give as the complete formula, which represents the effect of temperature on conductivity,

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0} (1 + \beta t)^n e^{-at}.$$

At low temperatures negative temperature coefficients have been found in very few instances. As was stated before, we have found *negative* temperature coefficients in the case of cobalt chloride in acetone; in a 75 per cent mixture of acetone with methyl alcohol; also in 50 and 75 per cent mixtures of acetone with ethyl alcohol. In the 75 per cent mixture of acetone with methyl alcohol, at the dilution $v=200$, we have practically *no temperature coefficient of conductivity*. In all

¹ P. Roy. Soc., 71, 42 (1902).

² Beibl., 16, 182 (1892).

cases these negative coefficients were found while working at ordinary temperatures.

Acetone and the alcohols are considered to be highly associated compounds at ordinary temperatures. We have shown that the diminishing dissociating power of a solvent with rise in temperature must overcome the increasing velocities of the ions, in order to have a decrease in conductivity with rise in temperature. Acetone and the alcohols are more associated at 0° than at 25° and, consequently, their dissociating power is greater at the lower temperature. The ions, however, move faster at 25° than at 0° . Since we have found negative temperature coefficients, we believe that the effect due to diminishing dissociation more than overcomes the effect due to the increasing velocities of the ions.

We think, nevertheless, that there is another factor which comes into play. We are inclined to the view that the solvates which are formed in these cases may be more stable at the higher temperature and, therefore, we should expect the reaction which gave rise to it to be endothermic. At the dilution where the temperature coefficient of conductivity is practically zero, these *opposite influences which affect conductivity become equal*. The point where we have a temperature coefficient, which is practically zero, corresponds to the maximum in conductivity obtained by other workers at high temperatures.

Summary.

1. We have measured the fluidities of water, methyl alcohol, ethyl alcohol, acetone, and binary mixtures of these solvents; also the fluidities of solutions of lithium bromide in these mixtures.

2. We have also measured the conductivity of various concentrations of lithium bromide and cobalt chloride, in the above named solvents and mixtures of these with one another.

3. The conductivities, in the case of mixtures of the alcohols with water, exhibit a minimum. The same fact was found to be true in the case of mixtures of acetone with water. This minimum in conductivity was found to be more pronounced at the lower temperature, and has been shown to be

intimately connected with the minimum in fluidity observed in the above mixtures.

4. The conductivities of lithium bromide, in mixtures of methyl and ethyl alcohols, are what we should expect from the law of averages. The conductivity curves are nearly straight lines. In the case of cobalt chloride, in these mixtures, there was a slight sagging of the curves.

5. In the case of lithium bromide, in mixtures of acetone with the alcohols, the fluidities are what we should expect from the law of averages—the fluidity curves are straight lines. The same has been found to be true in the case of the pure solvents. This indicates that acetone and the alcohols do not form more complex aggregations when mixed than when unmixed. Here again, conductivity has been shown to be connected with fluidity.

6. Lithium bromide, however, gives a pronounced maximum in conductivity, in mixtures of acetone with methyl or ethyl alcohol. The same phenomenon was observed in the case of cobalt chloride in mixtures of acetone with ethyl alcohol. We believe this maximum is due, primarily, to a diminution in the dimensions of the atmosphere about the ions.

7. We think, also, that the changes in the size of the ionic spheres should be considered as a factor in causing the conductivity minimum as well as the maximum.

8. We have determined the temperature coefficients of conductivity and fluidity, and found them to be of the same order of magnitude. Lithium bromide, in the mixtures studied, showed, with rise in temperature, a large increase in conductivity, due to increase in fluidity. The temperature coefficients of lithium bromide in the above mixtures are, therefore, all positive.

9. Cobalt chloride, however, in some of the acetone mixtures, at *ordinary temperatures*, gave *negative temperature coefficients*. We think this is due not only to the effect of the diminishing dissociation more than overcoming the effect due to the increasing velocity of the ions, but also to the fact that the solvates formed in these cases may be more stable at the higher tem-

perature. We should, therefore, expect, the reaction which gave rise to the solvates to be endothermic.

10. We have found for our substances, in a given mixture of solvents, a dilution where the temperature coefficient of conductivity is practically zero. This corresponds to the maximum in conductivity observed by other workers at elevated temperatures.

11. We have shown that the temperature coefficients generally increase with the dilution, not only in aqueous solutions but also in the non-aqueous solutions thus far studied.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF BROMINE ON DIMETHYLANILINE.

[SECOND PAPER.]

BY C. LORING JACKSON AND LATHAM CLARKE.

In the year 1904 Dr. K. Fries published the first account¹ of an extended research on the action of bromine on aromatic amines. We had been studying the action of bromine on dimethylaniline for some months before the appearance of this paper and, as our observations led us to believe that our products belonged to a different class from the perbromides described by Dr. Fries, we decided that we could finish and publish our work without approaching too near to the field reserved by him. When Dr. Fries received our paper² he repeated our experiments and, although he followed our directions most carefully, obtained from them only a hydrobromide and perbromides identical with those prepared in his earlier work. With the greatest kindness he then wrote us an account of his results, and pointed out that they indicated we were mistaken in the constitution ascribed to our compounds. These are given in the following table, in which the first column gives the formulas as determined by us and the second the

¹ Ber. d. chem. Ges., **37**, 2338 (1904). For a full account of his work see "Habilitationsschrift," Marburg, 1905, or Ann. Chem. (Liebig), **346**, 128 (1906).

² THIS JOURNAL, **34**, 261 (1905).

formulas of the substances obtained by Dr. Fries when following the directions for our experiments :

Jackson and Clarke.	Fries.
1. $\text{Br}_2\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	$\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2 \cdot \text{HBr}$
2. $\text{Br}_2\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{Br}_2$	$\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2 \cdot \text{HBr}_3$
3. $\text{Br}_2\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2\text{Br}_2$	$\text{C}_6\text{H}_3\text{Br}_2\text{N}(\text{CH}_3)_2 \cdot \text{HBr}_3$

In our formulas the bromine is added to the benzene ring or the nitrogen of the amino group, in his the added bromine is attached to the bromine of the hydrobromide, making perbromides.

Our formulas depended on two observations, of which the most important was that when crystals of the first substance were mixed with ethyl bromide they became oily and, after the two liquids had stood in contact for a few minutes, crystals began to appear on the surface of the oil, which, after some hours, was almost completely converted into white, flat prisms mixed with a small amount of red substance. These crystals were dried on a porous plate and analyzed without further purification.

0.0663 gram substance gave 0.0955 gram AgBr.

Br	Calculated for $\text{Br}_2\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 \cdot \text{C}_2\text{H}_5\text{Br}$.	Found.
	61.54	61.27

Dr. Fries, on repeating the treatment of dimethylaniline with bromine, molecule for molecule, which gave us substance No. 1, obtained, even at -20° , only the hydrobromide of parabromdimethylaniline, $\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2 \cdot \text{HBr}$, identical with that made from hydrobromic acid and parabromdimethylaniline. This naturally led him to the conclusion that we had also obtained this substance and that our analysis of



given above—the only real proof that the substance had our formula—was due to some experimental mistake. He supported this view by pointing out that our analysis was made with a very small amount of substance, 0.0663 gram, and that our supposed quaternary ammonic bromide,



was decomposed by water instead of dissolving in it unaltered, as would be expected. If his view were correct, and our substance was a substituted hydrobromide, the further action of bromine upon it would give the perbromides 2 and 3 in the second column of the table, instead of the addition compounds, which we thought we had obtained (column 1).

Accordingly, after receiving Dr. Fries' letter, we repeated our experiments on the action of bromine on dimethylaniline, molecule for molecule, and, in the first two preparations, obtained parabromdimethylaniline, $C_6H_4BrN(CH_3)_2$, recognized by its melting point, 55° ; but our third experiment gave instead a viscous product, a portion of which, on treatment with ethyl bromide, yielded white crystals, and these, after drying on a porous plate, gave the following result on analysis:

0.3505 gram substance gave 0.5004 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2 \cdot C_2H_5Br$.	Found.
Br	61.54	60.75

This, by confirming our earlier analysis given above, and proving that this product is the quaternary ammonic bromide, disposes of Dr. Fries' suggestion that the mother substance was $C_6H_4BrN(CH_3)_2 \cdot HBr$, which could give no such product.

Although the differences in properties between Dr. Fries' hydrobromide, $C_6H_4BrN(CH_3)_2 \cdot HBr$, and our benzdibromide, $Br_2C_6H_5N(CH_3)_2$, are not great enough to prove alone that the substances are different, they are sufficient to support the proof derived from the action of ethyl bromide. Thus, our substance gives a reddish-brown color with a chloroform solution of quinone, whereas $C_6H_4BrN(CH_3)_2 \cdot HBr$ gives none, and the melting point of our crystals was 82° , whereas the hydrobromide melts at 105° , and, although it melts in the crude state at 80° – 90° , according to Dr. Fries, it seems hardly probable that such good crystals as those used by us should melt 20° below the proper temperature.

The compound $Br_2C_6H_5N(CH_3)_2 \cdot C_2H_5Br$ was decomposed by water, as observed by us previously, but we were unable to study this phenomenon as we wished, because we did not succeed in obtaining the benz-3,4-dibromide of dimethylaniline

again, 5 additional attempts to make it giving only the hydrobromide of parabromdimethylaniline, as in the experiments of Dr. Fries. This decomposition of the quaternary ammonic bromide by water is not, however, so strange as appears at first sight. Dr. Fries¹ has shown that orthoparadibromdimethylaniline does not combine with methyl iodide to form a quaternary ammonic iodide, nor could he obtain an addition even by the use of dimethyl sulphate. It would be expected, therefore, that the quaternary ammonium derivative of our substance, which also contains 2 atoms of bromine, would be so unstable as to be decomposed by water.

The remainder of the benz-3,4-dibromide of dimethylaniline, made in our third preparation, was used in testing the second observation on which the constitution of our compounds depends. For this purpose it was converted by the further action of bromine into the compound $\text{Br}_2\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2\text{Br}_2$, No. 3 column 1 of the table, which, according to our earlier experiments, gave with sodic acetate and acetic acid only orthoparadibromdimethylaniline, $\text{C}_6\text{H}_3\text{Br}_2\text{N}(\text{CH}_3)_2$, whereas Dr. Fries' perbromide, $\text{C}_6\text{H}_3\text{Br}_2\text{N}(\text{CH}_3)_2\cdot\text{HBrBr}_2$, No. 3 column 2, gives² a mixture of orthoparadibromdimethylaniline and tribrommonomethylaniline, $\text{C}_6\text{H}_2\text{Br}_3\text{NHCH}_3$. Upon treating our new sample of the Br_5 compound with anhydrous sodic acetate, in acetic acid, an oily product was obtained which was dissolved in acetone and saturated with gaseous hydrobromic acid, the precipitate formed melted, without recrystallization, at 110° . The filtrate from this precipitate was freed from acetone by evaporation, and the residue also melted, without recrystallization, at 110° . As the orthoparadibromdimethylaniline hydrobromide, $\text{C}_6\text{H}_3\text{Br}_2\text{N}(\text{CH}_3)_2\cdot\text{HBr}$, melts at 110° and the tribrommethylaniline hydrobromide, $\text{C}_6\text{H}_2\text{Br}_3\text{NHCH}_3\cdot\text{HBr}$, at 202° , this experiment shows that none of the latter substance was present and, consequently, that our compound containing Br_5 is different from Fries' perbromide with a similar composition. Our later experiments, therefore, have established the accuracy of the two observations, on which the constitution of our 3 addition products rests.

¹ "Habilitationsschrift," p. 67. *Ann. Chem. (Liebig)*, **346**, 190.

² "Habilitationsschrift," p. 75. *Ann. Chem. (Liebig)*, **346**, 199.

The most interesting result of this later work is that a mixture of dimethylaniline bromine and chloroform may give 2 entirely different products, when there is no apparent difference in the conditions of the reaction; thus, sometimes the addition product, $\text{Br}_2\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, was formed as in our earlier and one of our later experiments; at other times the substitution product, $\text{C}_6\text{H}_4\text{BrN}(\text{CH}_3)_2 \cdot \text{HBr}_2$, as in Dr. Fries' work and 5 of our later experiments.

In the following consideration of the conditions of these reactions we are able to show that most of them did not cause this variation in the results. It could not be due to slight differences in the purity of the dimethylaniline or the bromine, as all of our 8 later experiments were tried with the same materials, and 7 yielded the substitution and the addition product. The chloroform used in all these experiments also came from the same specimen, but, as it was allowed to stand over calcic chloride during the work, the samples used in the last preparations may have been drier than those used for the earlier ones. In fact, in our first 2 preparations, the product was parabromdimethylaniline, due, perhaps, to the presence of some water; in the third the addition product was formed; and in the 4th, 5th, 6th and 8th, when the solvent was thoroughly dry, parabromdimethylaniline hydrobromide. It was possible, therefore, that the intermediate amount of moisture still present in Experiment 3 might have been the cause of the formation of the addition product. This theory seems improbable on its face, because the presence of water, with its strong attraction for hydrobromic acid, should promote substitution rather than addition, but we thought it important enough to test experimentally and, accordingly, experiment 6 was tried with the dry chloroform, experiment 7 with the same chloroform, to which a little washed chloroform had been added in order to make it slightly moist. As both these experiments gave parabromdimethylaniline hydrobromide, the difference in behavior can hardly be due to traces of moisture.

If the difference depended on a gradual decomposition of the chloroform during the series of experiments, those tried at first

would have given one result, those later the other, but, in fact, both the first and last preparations gave substitutions, the addition occurring in the third experiment. It would seem, therefore, that this possible cause must be rejected. We may add that the chloroform was kept in the dark and showed no sign of decomposition so far as one could tell by its odor.

The results cannot be due to differences in the length of the action, as it was essentially the same in all cases; nor to differences in the intensity of the sunlight, as the addition compound could also be obtained in diffused daylight; nor to differences in temperature, as Dr. Fries obtained substitution at a temperature of -20° . The proportion of the two reagents also did not influence the result, as we have obtained additions with 1, 2 or 3 molecules of bromine to each molecule of dimethylaniline.

We have been able to find only one possible cause for these differences, which has not been eliminated in the previous discussion, but, as our inability to make the addition products at present has prevented us from testing this hypothesis experimentally, we would mention it only as an indication of the direction in which future experiments will be tried in this laboratory. This hypothesis is that the air of a laboratory, in which hydrobromides or perbromides have been made, becomes filled with these substances in the form of impalpable dust, which inoculates the solutions and thus leads to the formation of substitution instead of addition products. This would explain the impossibility of obtaining additions in Dr. Fries' laboratory, and the facts that our first experiments led to additions as the rule, but, after we had made a number of perbromides, it became increasingly difficult to obtain addition products, and in our last experiments in only one case out of eight was there addition. Arrangements have been made to test experimentally the possibility of such inoculations by minute quantities of a substance,¹ and we hope in this way to arrive at a real knowledge of the cause of these strange differences in behavior.

CAMBRIDGE, MASS.,
June 1, 1906.

¹ Cf. Ostwald: *Z. physik. Chem.*, **22**, 289.

REVIEWS.

A SHORT MANUAL OF ANALYTICAL CHEMISTRY, Qualitative and Quantitative,—Inorganic and Organic. By JOHN MUTER, PH.D., F.R.S.E., F.I.C., F.C.S., etc. Fourth American edition, illustrated. The chapters relating to the analysis of drugs being based upon the eighth revision (1905) of the United States Pharmacopœia. Philadelphia: P. Blakiston's Son & Co. 1906. Price, \$1.50.

The appearance of a new edition of this well-known manual of analysis for pharmacists and physicians shows that it is a favorite. It is deservedly so. In brief, compact form the book treats of the detection of metals, the detection and separation of acids, of qualitative analysis and quantitative analysis, volumetric and gravimetric, of organic analysis, of special processes for the analysis of air, water, food, drugs and urine, and of gas analysis.

The author says that the chapters on gravimetric and gas analysis are only introductory; with these exceptions the treatment is remarkably complete, though purely empiric. It is not suited to students of chemistry, but is well adapted to those who, with a slight knowledge of chemistry, need reliable instruction in analysis as a tool of their profession. F. R.

CHEMISTRY OF THE PROTEIDS. By GUSTAV MANN, M.D., B.Sc. University Demonstrator of Physiology, Oxford. Based on PROFESSOR OTTO COHNHEIM'S "Chemie der Eiweisskörper." London: Macmillan & Co. 1906. pp. 606. Price, \$3.25.

This work consists largely of a translation of Cohnheim's "Chemie der Eiweisskörper." The author has introduced a considerable quantity of new matter, especially in the part dealing with colloidal solution, where he frequently refers to his book on "Physiological Histology." He attaches too much chemical significance to his histological work. Many of his expressions may cause some confusion if used by students; thus, he repeatedly refers to the decomposition products of the proteids as "dissociation products." Such statements as the following occur throughout the book: In the preface the author states, "A new view has been advanced, namely, that so-called neutral salts are, as a matter of fact, not neutral, for it is their very want of neutrality which allows them to dissolve in water, and which also enables them to dissolve globulins or to keep these compounds in solution." For this reason the reviewer thinks it is not a desirable book to be placed in the hands of the average student. It contains a good bibliography, however, and is a handy work for the specialist who can overlook such errors as would confuse and mislead a beginner.

A. S. L.

THE DYNAMICS OF LIVING MATTER. By JACQUES LOEB, Professor of Physiology in the University of California. The Columbia University Press: The Macmillan Company, Agents. 1906. pp. 233. Price, \$3.00.

To any one who has followed the beautiful experiments of Loeb on artificial parthenogenesis, this volume will be most welcome. The author states in his preface that this book "owes its origin to a series of 8 lectures delivered at Columbia University in the spring of 1902." An idea of the scope of the book can be gained by brief reference to the chapter headings. These are: Concerning the General Chemistry of Life Phenomena; The General Physical Constitution of Living Matter; On Some Physical Manifestations of Life; The Rôle of Electrolytes in the Formation and Preservation of Living Matter; The Effects of Heat and Radiant Energy upon Living Matter: Heliotropism; Further Facts Concerning Tropism and Related Phenomena; Fertilization; Heredity; On the Dynamics of Regenerative Processes.

This book is of interest to the chemist and physicist, as well as the biologist; since, as the author points out, "To-day every one who is familiar with the field of chemical biology acknowledges the fact that the chemistry of living matter is not specifically different from the chemistry of the laboratory." And again, "The phenomena which allow us to discriminate between dead and living matter are physical processes, *e. g.*, in higher animals, the contraction of the heart, the respiratory and other muscular motions. If the chemical process in living matter and the physical changes they bring about in the colloids were entirely known, the physical manifestations of life would also be clear to us."

It is well known that Loeb is one of the pioneers in introducing physical chemistry into physiology, and his chapter on the "Rôle of Electrolytes in the Formation and Preservation of Living Matter" is of special interest to physical chemists. The significance of physical chemistry for physiology and its direct bearing on that science are shown by the following sentence alone: "Not only the life of the aquatic animals, but the life of every cell is passed in a solution of electrolytes."

The chapter to which we naturally turn with greatest interest is that which has to do with "Fertilization," since it is especially in this field that Loeb has done so much, and such brilliant work. It is well known that Loeb has caused the unfertilized eggs of sea urchins to develop, by simply placing them in sea-water made more concentrated by the addition of sodium chloride, and has studied the difference between the larvae thus produced and those resulting from eggs fertilized

normally by means of sperm. It would lead too far, in the present connection, to discuss in detail these elaborate investigations; suffice it to quote the following sentence near the close of this chapter: "I am inclined to believe that the direct and essential effect of the spermatozoön and the methods of artificial parthenogenesis is the starting of a definite chemical process."

To one who is interested in such problems primarily from the purely chemical and physical side, it seems that this work of Loeb opens an entirely new field.

H. C. J.

CHEMISTRY OF THE ALBUMENS. By S. B. SCHRYVER, D.Sc., Ph.D., Lecturer in Physiological Chemistry to University College, London. Published under the auspices of the University of London. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 192. Price, \$2.00.

The author here presents, in the form of 10 lectures, an excellent, readable and fairly complete resumé of the subject of proteid chemistry as it stands to-day. The great progress which has been made in this important field within the last decade is here presented in a clear, concise way which a student can readily grasp. The whole merit of the book lies in the first 8 lectures, which deal with the purely chemical aspect of the subject. The last 2 lectures consist, as the author states in the preface, of a very incomplete, critical review of the theories which have been advanced to explain the differences between living and dead matter and the nature of metabolism. In the first 8 lectures the constitution and synthesis of the decomposition products of the proteids and the synthesis of the polypeptides are dealt with in a very satisfactory manner. The work of Curtius is, however, not mentioned. The book is to be cordially recommended.

A. S. L.

GRUNDRISS DER ELEKTROCHEMIE. Von DR. HANS JAHN, Professor an der Universität Berlin. Zweite umgearbeitete auflage, mit 5 abbildungen im Texte. Wien: Alfred Hölder. 1905. pp. 549. Price, M. 17.20.

Although this is called a second edition of Jahn's work, it is so thoroughly revised as to be practically a new book. The preface to the first edition contains such a number of valuable points that every one is urged to read it carefully. Not least important among the many admirable suggestions contained in this preface is that which bears upon the absolute necessity of chemists becoming familiar with the elements of higher mathematics.

As Jahn states, "Just as to-day every physicist must become familiar with mathematics in order to understand the theoretical side of his branch of science, so also, to the chemist who is not familiar with the elements of higher analysis,

the theoretical side of his subject will remain a book with seven seals.

"The progress that has been made in this direction, in recent times, is, on the whole, satisfactory. Through the introduction of physical-chemical methods into organic and inorganic chemistry, the application of mathematical analysis to these branches of natural science has been made possible.

"The elements of higher mathematics are to-day just as essential to any one who would understand the science of chemistry, in contradistinction to the great mass of more or less disconnected facts that have been accumulated during a century, as they are to the physicist, and the time is near at hand when no one can enter the field of chemistry primarily because it requires no mathematics."

The book under review is rather one of reference than a text-book. It contains 4 large sections: The Fundamental Laws of Electrochemistry; The Theory of Electrolytic Dissociation and Some of Its More Important Consequences; The Transformations of Energy in Electrochemical Processes; and Galvanic Polarization.

Whether used as a book of reference or as a text-book, this is an advanced work on electrochemistry. Its chief fault is one of omission—and the omission especially of work not published in German journals. This is becoming a common fault of German scientific treatises, and a serious fault it is. The general value of the works in which it exists is greatly lessened.

The electrochemistry by Jahn will undoubtedly find a place in every chemical and physical library, as well as in every laboratory where physical chemistry is taught. H. C. J.

DAS NEUE TECHNISCH-CHEMISCHE INSTITUT DER KÖNIGLICHEN TECHNISCHEN HOCHSCHULE ZU BERLIN UND DIE FEIER SEINER ERÖFFNUNG AM 25 NOVEMBER, 1905. Von dem Direktor des Instituts, DR. OTTO N. WITT, Geheimer Regierungsrat und Professor. Berlin: Weidmannsche Buchhandlung. 1906. pp. 38. Price, M. 2.

This is a reprint, admirably and copiously illustrated, of Professor Witt's address which has been already fully reported upon in this JOURNAL by Professor Renouf.¹ J. B. T.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1905. Issued by the Chemical Society. London: Gurney & Jackson. 1906. pp. 340. Price, 4 shillings and 6 pence, net.

The volume for 1905 maintains the standard of the volume for 1904; the statements are clear, their brevity is extreme. The last number of the Jahrbuch der Chemie, which covers the same ground, has 590 pages; as a guide for literature reference the one is as valuable as the other. E. R.

¹ THIS JOURNAL, 35, 358 (1906).

AMERICAN CHEMICAL JOURNAL

Contribution from the Laboratory of the Bureau of Internal Revenue, U. S. Treasury Department.

THE CRYSTALLINE APPEARANCE OF CALCIUM TARTRATE AS A DISTINCTIVE AND DELI- CATE TEST FOR THE PRESENCE OF TARTARIC ACID OR TAR- TRATES.

BY A. L. SULLIVAN AND C. A. CRAMPTON.

The necessity of ascertaining the presence of tartaric acid in connection with the study of the composition of various fruit syrups, ciders, compound wines, baking powders, etc., makes desirable a reliable method for its detection.

A method is described below which has given very satisfactory results, proving, on the whole, more reliable than the identification by means of the precipitation of the acid potassium tartrate, or by the silver nitrate reduction test.

Use is made of the familiar reaction of tartrates with calcium chloride. Soluble tartrates, when treated with calcium chloride, give a precipitate of calcium tartrate which becomes crystalline on standing, the precipitate forming in dilute solutions only after some hours.

With the aid of the microscope the above reaction furnishes the basis for a delicate test for tartaric acid in various substances.

By experiment it was found that when a solution containing tartaric acid in small amount, was treated as described below, crystals of calcium tartrate, in the form of rhombic prisms or pyramids, separated out. These crystals are readily recognized under a low power microscope, magnification 75 to 100 diameters, and are characteristic of tartaric acid.

Preparation of Solution.

(1) The solution to be tested should be concentrated to a small bulk. In the case of fruit juices, wine and ciders, when the amount of tartaric acid is thought to be very small, 150-200 cc. may be evaporated to 50 cc. The solution, after concentration, should not contain more than 30 per cent of solid matter, sugar, dextrin, glycerin, etc.

(2) In the case of fruit syrups of high content of solids, it is advisable to precipitate the organic acids with lead subacetate, and after decomposing the precipitate with hydrogen sulphide, to make use of the concentrated solution containing the acids.

Method of Procedure.

The solution of about 50 cc. prepared by (1) or (2), according to the nature of the sample, is cooled and made slightly alkaline with potassium hydroxide, a few drops of potassium acetate, 20 per cent solution, is added and, after acidify ~~ing~~ ^{ing} with acetic acid, about 10 cc. of calcium chloride, 30-40 per cent solution, added, and the whole stirred rapidly for a minute or two. After standing at room temperature for 12-15 hours, the solution may be decanted off and the crystals of calcium tartrate, if present, will be seen in the bottom of the beaker. These, under the microscope, appear as characteristic prisms, similar to those in Plate I. The crystals vary a great deal in size, according to the amount of tartaric acid present in the solution.

As a rule, when only a small amount is present, the crystals are approximately the size of those shown in Plate I. When

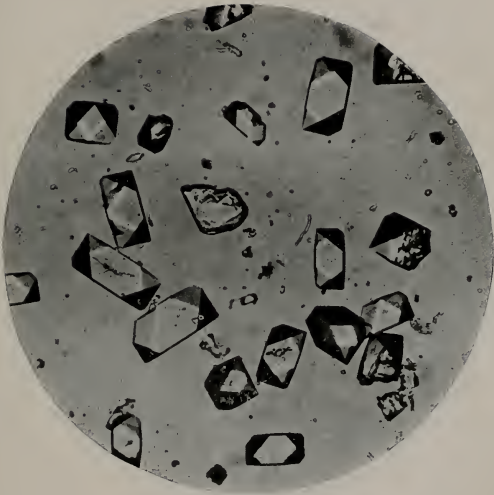


Plate I.

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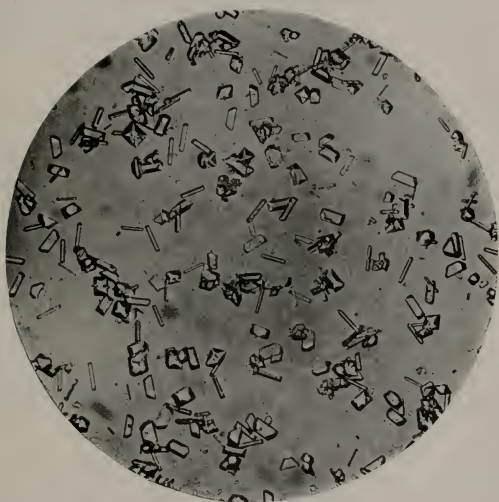


Plate II.

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sufficient tartaric acid is present so as to be precipitated within an hour or two, the crystals resemble in size and shape those in Plate II. Isolated prisms of a smaller size, but of identical shape as those in Plate I., will be readily observed.

In the examination of compound ciders and fruit juices, if tartaric acid is present in sufficient quantity to give a crystalline precipitate in a few minutes, and the crystals are not characteristic, it is advisable to make a new test, using less of the sample. Crystallization from a dilute solution gives more characteristic crystals, as noted above.

Tartaric Acid in Succinic Acid.

Five per cent of tartaric acid in succinic acid may be readily detected.

Two grams of succinic acid should be dissolved in 40 cc. of water, and after neutralizing with potassium hydroxide, a few drops of potassium acetate are added, then 10 cc. calcium chloride solution and 3 cc. glacial acetic acid.

Tartaric acid, if present in quantity equal to 5 per cent, will give crystals of calcium tartrate similar to those in Plate I., after standing for several hours.

Study was made of the following substances: Tartaric acid, wine, citric, malic, succinic, oxalic and aconitic acids.

The effect of the addition of mineral acids was also noted.

Experiments with Wine.

Several tests of the method were made with different wines, containing varying amounts of tartaric acid.

Characteristic crystals of calcium tartrate were obtained with wine diluted to 50 cc. and containing as low as 0.05 gram of total tartaric acid. A wine containing 39 per cent of solids, consisting of the natural solids and added sugar and glycerin, and 0.0625 gram of total tartrates in 50 cc. of solution, gave positive results.

Tartaric Acid—The following tests were made with tartaric acid :

Tartaric acid.	Volume of solution.	Remarks.
0.05 gram	50 cc. of water	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (25 per cent solids, sugar and glycerin)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (10 per cent solids, cane sugar)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (35 per cent solids, sugar)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (26 per cent solids, equal parts of glycerin and sugar)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (50 per cent sugar solution)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (50 per cent glycerin solution)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (45 per cent solids, 25 per cent sugar and 20 per cent glycerin)	Characteristic crystals of calcium tartrate

Oxalic Acid.—Oxalic acid gives a precipitate of calcium oxalate with calcium chloride, but this precipitate does not resemble the calcium tartrate. When tartaric acid is present with the oxalic acid, crystals of calcium tartrate will be found floating on the top of the solution. These may be gathered on a stirring rod, placed on a slide and examined under the microscope.

Tartaric and oxalic acids.	Volume of solution.	Remarks.
0.1 gram tartaric acid + 1.0 gram oxalic acid	50 cc. of water	Crystals of calcium tartrate present
0.05 gram tartaric acid + 0.5 gram oxalic acid	50 cc. of water	Crystals of calcium tartrate present

Succinic Acid.—Tests were made with succinic acid, as follows :

Succinic acid.	Volume of solution.	Remarks.
1 gram succinic acid	50 cc.	No precipitate
1 gram succinic acid + 0.05 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained
2 grams succinic acid + 1 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained

In these tests with succinic acid 3 cc. of acetic acid were added to the solution after the addition of the calcium chloride.

Citric acid.	Volume of solution.	Remarks.
1 gram citric acid	50 cc.	Heavy precipitate of calcium citrate. Acetic acid was added to similar solutions, in amount varying from 1 to 5 cc., but beyond making the precipitate in the form of a crust, there was no other effect
0.5 gram citric acid 0.1 gram tartaric acid	50 cc.	Heavy precipitate of calcium citrate. A few crystals of calcium tartrate were observed after standing for 2 hours
0.1 gram citric acid 0.1 gram tartaric acid	50 cc.	Heavy precipitate of calcium citrate. A few crystals of calcium tartrate were observed after standing for 2 hours
0.1 gram citric acid + 0.05 gram tartaric acid	50 cc.	Precipitate of calcium citrate, test negative

Owing to the precipitation of calcium citrate when citric acid is present in greater quantity than tartaric acid, the form of the calcium tartrate crystals is changed and the test is liable to fail. If the precipitate, or some of the crystals obtained, are dissolved in a small amount of nitric acid and the calcium precipitated with sodium carbonate, the filtrate containing the tartaric and citric acids will give a silver mirror with the silver nitrate reduction test. Neither malic, citric, nor succinic acids reduce the silver nitrate and form a mirror.

Malic Acid.—

Malic acid.	Volume of solution.	Remarks.
1 gram malic acid	50 cc. water	No precipitate
1 gram malic acid + 0.05 gram tartaric acid	50 cc. water	Plates and needles. Calcium tartrate crystals are not characteristic as in Plate I.
0.5 gram malic acid + 0.1 gram tartaric acid	50 cc.	Plates and needles. Calcium tartrate crystals are not characteristic as in Plate I.

Malic acid gives no precipitate with calcium chloride. If it be present with tartaric acid it modifies the form of the calcium tartrate crystals. One having had considerable experience with the method would recognize the trouble, but it is safer to confirm the test by means of the silver nitrate reduction test, as described under citric acid.

Aconitic acid.	Volume of solution.	Remarks.
0.5 gram aconitic acid 0.1 gram tartaric acid	50 cc.	Characteristic crystals of calcium tartrate, although rather small in size
0.25 gram aconitic acid 0.1 gram tartaric acid	50 cc.	Characteristic crystals of calcium tartrate, although rather small in size

Tartaric and sulphuric acids.	Volume of solution.	Remarks.
0.1 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained
0.1 gram sulphuric acid		
0.1 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained
0.25 cc. conc. sulphuric acid		
2 grams tartaric acid	50 cc.	Crystals of calcium tartrate obtained
0.5 cc. conc. sulphuric acid		
2 grams tartaric acid	50 cc.	Result doubtful
1 cc. conc. sulphuric acid		

Alum and tartaric acid.	Volume of solution.	Remarks.
0.1 gram alum	50 cc.	Negative
0.5 gram tartaric acid		
0.1 gram alum	50 cc.	Negative
0.1 gram tartaric acid		

Mixtures.	Volume of solution.	Remarks.
0.5 gram citric acid	50 cc.	Precipitate of feathery tufts with a few large crystals of calcium tartrate
0.5 gram succinic acid		
0.1 gram tartaric acid		
0.5 gram citric acid	50 cc.	A precipitate of plates. Negative test. Presence of tartaric acid confirmed by the silver nitrate reduction test
0.3 gram malic acid		
0.1 gram tartaric acid		
0.1 gram malic acid	50 cc.	Crystals of calcium tartrate
0.1 gram citric acid		
0.1 gram succinic acid		
0.075 gram tartaric acid	50 cc.	Negative. Presence of tartaric acid confirmed by silver nitrate reduction test
0.5 gram malic acid		
0.5 gram succinic acid		
0.05 gram tartaric acid	50 cc.	Crystals of calcium tartrate
0.05 gram potassium sulphate		
0.1 gram tartaric acid		
1.5 grams potassium chloride	50 cc.	Crystals of calcium tartrate

Conclusion.

The calcium tartrate crystals obtained by the method described above are characteristic for tartaric acid. None of the other organic acids gave crystals of a similar form with calcium chloride. When crystals, as shown in Plate I. or II., are obtained, positive conclusion is warranted that tartaric acid is present.

Citric and oxalic acids give a precipitate with calcium chloride; malic acid does not, but if present with tartaric acid, the form of the calcium tartrate crystals is changed, the crystals being in the form of plates and needles. It is believed that the mixtures containing tartaric and other acids which failed to give satisfactory tests with the method represented extreme cases, and that under ordinary conditions the method is reliable. The precipitation of tartaric acid as the bitartrate proved even more liable to failure than the precipitation as calcium tartrate.

In cases where a precipitate is obtained with calcium chloride, and no characteristic crystals of calcium tartrate can be observed, the presence or absence of tartaric acid may be proved, as follows:

Wash the precipitate with 50 per cent alcohol and dissolve in a small amount of nitric acid. Precipitate the calcium with sodium carbonate, to the filtrate add ammonia and a crystal of silver nitrate and heat in a test tube. A silver mirror will be obtained if tartaric acid is present.

The presence of alum, or of an excess of mineral acids interferes with the test, preventing the precipitation of calcium tartrate.

From a large number of experiments with the test, conclusion is warranted that it is a convenient and reliable method for detecting tartaric acid in wines, ciders, fruit syrups, etc., and it is believed to be possible to adapt it to other substances as occasion may arise.

THE RELATIVE MIGRATION VELOCITIES OF THE
IONS OF SILVER NITRATE IN WATER, METHYL
ALCOHOL, ETHYL ALCOHOL AND ACETONE,
AND IN BINARY MIXTURES OF THESE
SOLVENTS, TOGETHER WITH THE
CONDUCTIVITY OF SUCH SOLU-
TIONS.

BY HARRY C. JONES AND CHARLES A. ROUILLER.

PART I.

HISTORICAL SKETCH.

1. *Earlier Observations.*

Shortly after solutions began to be subjected to the action of the current from the voltaic pile, it was noticed that changes were produced at the poles. Carlisle¹ observed that in the decomposition of water alkali was formed at the cathode. This was later proved by Davy² to be due to the presence of saline impurities in the water. In the meantime it had been shown that this decomposition of salts, and the transference of the base to the negative pole and the acid to the positive electrode, was general, and Berzelius and Hissinger³ proposed their famous electrochemical theory.

About 30 years later Faraday⁴ performed some experiments to show that the passage of a current through a solution produces changes in concentration about the poles. Gmelin⁵ observed that when a solution of copper sulphate is electrolyzed between copper electrodes, it becomes colorless at the cathode, while the blue color about the anode increases in intensity. Pouillet⁶ found a similar change in concentration in a gold chloride solution.

In 1844 Daniel and Miller,⁷ continuing the earlier experi-

¹ Nicholson : Gilbert's Ann., 6, 340 (1800). Ostwald : "Elektrochemie," p. 130.

² Phil. Trans., 1807, p. 1. Ostwald's "Klassiker," No. 45.

³ Jour. d. Chem., 1, 115 (1803). Ostwald : "Elektrochemie," p. 317.

⁴ Pogg. Ann., 32, 401 (1834).

⁵ *Ibid.*, 44, 1 (1838).

⁶ Compt. rend., 20, 1544 (1845).

⁷ Phil. Trans., 1844, p. 1.

ments of Daniel,¹ made it clear that different ions do not travel with the same velocity. They electrolyzed solutions of various salts in a cell divided into compartments by porous membranes. Their experimental errors were so great, however, that they reached the erroneous conclusion that certain ions, such as those of copper and zinc, do not migrate at all.

Smee² performed many experiments which showed that the electric current causes changes in concentration, but he still advocated the Faraday theory of electrolysis.

2. Hittorf and His Method of Determining Transport Numbers.

The true explanation of these phenomena was finally offered by Hittorf,³ in 1853. He showed that the changes in concentration about the poles were due to the fact that the anions and cations traveled with different velocities, and that the amount of the change was a measure of the relative velocities of the two ions. In this way he determined the transport numbers for a very large number of salts.⁴ He devised various forms of apparatus, depending on the nature of the salt under investigation, but all were of the same general type—a vertical tube divided into sections by porous diaphragms. The cathode was placed in the upper and the anode in the lower cell.

Working with solutions of copper sulphate, he found that the current density and the temperature, between 4° and 21°, had no measurable effect on the transport number, but that the relative velocity of the copper ion increased with the dilution until it reached a constant, maximum value. Extending his investigations to other salts, he found that in some the transport number did not change with the dilution; others acted like copper sulphate, and in still others such as silver nitrate, the relative velocity of the cation decreased as the dilution increased.

The various forms of apparatus which he employed all have some objectionable features. The use of membranes, espe-

¹ Phil. Trans 1839, p. 97; 1840, p. 209.

² Phil. Mag., 17, 193 (1840); 25, 434 (1844).

³ Pogg. Ann., 89, 177 (1853). Ostwald's "Klassiker," No. 21.

⁴ Pogg. Ann., 89, 1 (1856); 103, 1 (1858); 106, 337 (1859). Ostwald's "Klassiker," Nos. 21 and 23.

cially, may be a serious source of error. Hittorf¹ himself recognized this nearly 50 years later, and repeated many of his experiments, using silk web instead of animal membranes. He found that when solutions of alkali salts are forced by endosmose through porous diaphragms they are in no way changed, but solutions of the zinc and cadmium halides and many other electrolytes become more concentrated on the anode side, and the values obtained for the transport number of the cation are too low.

Hittorf's views met with extremely violent opposition, and for many years very little work was done in this field. Wiedemann,² in the course of his investigations on endosmose, measured the changes in concentration produced in various solutions by electrolysis. His apparatus consisted of two cylinders into which dipped glass tubes connected by rubber tubing.

Wieske³ determined a few transport numbers in an apparatus made of two bottles of known volume, connected near the top by a lateral tube. To separate the solutions after electrolysis, this tube was provided with a glass stop-cock.

Burgoin⁴ electrolyzed many organic acids and their salts, and studied quantitatively the products of decomposition. His apparatus consisted of two test-tubes, one inside the other, and communicating only by means of a small hole bored in the bottom of the smaller one.

Kirmis⁵ modified the Wiedemann apparatus by substituting glass for the rubber connections.

About this time F. Kohlrausch,⁶ as the result of a long series of conductivity measurements, was able to point out a close relationship between the velocities of ions and the conductivities of solutions. He showed that, in dilute solutions, under a given electromotive force, every ion moves through the liquid with a fixed velocity, dependent on its chemical nature but independent of the other ions. The conductivity, then, may be represented as the sum of two factors, related to each

¹ *Z. physik. Chem.*, **39**, 613 (1902); **43**, 239 (1903).

² *Pogg. Ann.*, **99**, 177 (1856).

³ *Ibid.*, **103**, 466 (1858).

⁴ *Ann. Chim. Phys.* [4], **14**, 157 (1868); [4], **21**, 264 (1870); [4], **22**, 361 (1871).

⁵ *Wied. Ann.*, **4**, 503 (1878).

⁶ *Ibid.*, **6**, 1, 145 (1879).

other as the transport numbers of anion and cation. If the constant maximum conductivity and the transport numbers are known, the absolute velocity of either ion can be easily calculated.

This did not at once lead to increased activity in the determination of transport numbers. Kuschel¹ and Lenz² investigated a few salts, using a slightly modified form of the Hittorf apparatus.

In 1888, wishing to test further Kohlrausch's law, Loeb and Nernst³ devised an apparatus for determining transport numbers, which did away entirely with porous diaphragms. It was essentially a Gay-Lussac burette provided near the top with a side tube for the reception of the cathode. Instead of the usual silver voltameter, they employed a galvanometer and Clark element in measuring the current. They determined the transport number of the silver ion in 8 salts and calculated its absolute velocity from their conductivity measurements. They found that the velocity, as calculated from the various salts, was constant to within the limits of experimental error.

The work of Chassy⁴ needs only to be mentioned. Kistiakowsky,⁵ in his determinations of transport numbers, used an extremely simple form of apparatus. It consisted merely of a vertical tube with a double bend near the top. His volt-meter is distinctive, the current being measured by determining volumetrically the amount of metal that had been dissolved from a silver anode.

Bein⁶ carried out quite an extensive investigation on the effect of membranes and of temperature on transport numbers. He found that porous clay plates had no effect on the relative velocities of the ions, but that fish bladder retarded the cation. With increase in temperature the ions tend to move with equal velocities.

Lusanna⁷ devised an apparatus of an entirely new form.

¹ Wied. Ann., **13**, 289 (1881).

² Mem. Acad. Imp. St. Petersb., [7], **30** (1882).

³ Z. physik. Chem., **2**, 948 (1888).

⁴ Ann. Chim. Phys., [6], **21**, 241 (1890).

⁵ Z. physik. Chem., **6**, 97 (1890).

⁶ Wied. Ann., **46**, 29 (1892).

⁷ Att. Ist. Ven., [7], **3**, 1111 (1892); [7], **4**, 1568 (1893).

Three bulbs were connected by bent tubes in such a way as to form an S, and the whole apparatus, after being filled, was laid in the bath horizontally.

Rosenheim,¹ studying the composition of complex salts, subjected their solutions to electrolysis in two U-tubes connected by a rubber tube. Gordon² showed that the temperature coefficient of the transport numbers of cadmium sulphate and bromide is zero.

Schrader³ and Hopfgartner⁴ electrolyzed mixtures of salts and acids, to determine the relative velocities of different anions or cations.

Bein⁵ again took up the problem and carried out a very elaborate series of investigations. He studied the effects of temperature and of concentration on the transport numbers of a large series of salts. He also gave special attention to the determination of the influence of dividing membranes. He found that, in general, they retarded the cation. From experiments with clay, parchment paper, fish bladder and gold beater's skin, he showed that the greatest change in velocity was produced by animal membranes, while porous clay divisions are almost without influence. He describes 5 forms of apparatus, all very complex.

Starck,⁶ finding that the Hittorf apparatus with dividing membrane was not suitable for his purpose—the determination of the transport numbers for strong sulphuric acid—devised a simpler form, consisting of 3 U-tubes, connected by bent glass tubes.

In order to determine whether ternary electrolytes dissociate into complex ions, Noyes⁷ made very careful determinations of the transport numbers for potassium sulphate and barium chloride and nitrate, in 0.1 N and 0.2 N solutions. He concluded that, even in the more concentrated solutions of potassium sulphate and barium nitrate, there are practically

¹ Z. anorg. Chem., 11, 225 (1896).

² Z. physik. Chem., 23, 469 (1897).

³ Z. elek. Chem., 3, 498 (1897).

⁴ Z. physik. Chem., 25, 115 (1898).

⁵ *Ibid.*, 27, 1 (1898); 28, 439 (1899).

⁶ *Ibid.*, 29, 385 (1899).

⁷ J. Am. Chem. Soc., 23, 37 (1901).

no complex ions, while barium chloride solutions show evidence of the presence of considerable numbers of complex anions. In his investigation he used an apparatus consisting essentially of two U-tubes connected by rubber tubing.

Pfanhauser,¹ Rieger² and Bukschnewski³ made some determinations of transport numbers. Pfanhauser was investigating the properties of nickel ammonium sulphate and used the Hittorf apparatus. Rieger, to study the electrolytic decomposition products of various complex salts, devised a rather complicated cell which, however, made possible a complete separation of the cathode and anode solutions after electrolysis.

Notwithstanding all the work that had been done in this field, all forms of apparatus thus far devised possessed very objectionable features. The solutions around the electrodes were kept separated by porous diaphragms, or by differences in specific gravity, and it was impossible to effect complete separation. Some of the most serious defects were overcome by Mather,⁴ working with Jones, who used essentially an M-shaped tube divided into two equal compartments by a stop-cock of large bore. He made a few determinations of the transport numbers for silver nitrate and acetate and obtained satisfactory results.

Jahn⁵ and his pupils undertook an extensive study of the effect of dilution on transport numbers. Their apparatus was quite similar to that of Hopfgartner. An Erlenmeyer flask served as anode compartment, while the cathode dipped into the further limb of a U-tube connected with a flask near the top of a lateral tube. They investigated solutions ranging in dilution from N/2 to N/300, of hydrochloric and nitric acids, silver nitrate, copper and cadmium sulphates, and the halogen salts of the alkalis, the alkaline earths and cadmium. They found that, in general, the transport numbers for most of the salts they studied reached a maximum, constant value at comparatively low dilutions. The relative

¹ Z. elek. Chem., **7**, 698 (1901).

² *Ibid.*, **7**, 863 (1901).

³ Dissertation, Berlin, 1901.

⁴ THIS JOURNAL, **26**, 473 (1901).

⁵ Z. physik. Chem., **37**, 673 (1901).

velocity of the silver ion in the nitrate was practically constant between N/30 and N/214. The copper ion in copper sulphate increased in velocity as compared with the anion, but reached its maximum relative speed in a N/12 solution. The transport numbers for the cadmium salts, as had already been shown some time previously by Hittorf, changed rapidly with the concentration.

Owing to the limited capacity of their apparatus, they were unable to work with any high degree of accuracy with solutions more dilute than N/150. Steele and Denison,¹ however, shortly afterwards devised an apparatus in which they could electrolyze unlimited amounts of solution. It was very similar to the form used by Noyes, but was connected at the top with a reservoir from which fresh solution could be supplied as the electrolyzed portions were drawn off at the bottom. They worked with calcium sulphate, nitrate and chloride, in solutions containing about 0.0045 gram-molecular weight of the salt to the liter. They found, from their transport number and conductivity measurements, that the velocity of the calcium ion was the same, whether determined from the chloride or the nitrate, while calcium and potassium chlorides gave concordant results for the velocity of the chlorine ion.

Among the more recent investigations may be mentioned those of Huybrecht² and Wolf.³ Both used the Hopfgartner-Jahn apparatus. Huybrecht studied magnesium sulphate and sulphuric acid. For this acid he found that the transport number of the hydrogen ion is constant for dilutions ranging between N/8 and N/80, and beyond N/105 it again has a constant, but somewhat higher value. Wolf obtained a negative temperature coefficient for the same ion in hydrochloric acid.

Noyes and Sammet⁴ made an accurate determination of the equivalent conductivity of hydrogen, by determining its transport number in hydrochloric acid. Using the same method with sulphuric acid, Tower⁵ finds that the relative velocity of

¹ J. Chem. Soc., 81, 456 (1902).

² Dissertation, Berlin, 1901.

³ *Ibid.*, 1903.

⁴ J. Am. Chem. Soc., 24, 944 (1903).

⁵ *Ibid.*, 26, 1039 (1904).

the anion increases markedly with dilution, from 1 N to 0.02 N solution, and has a large temperature coefficient between 8°, 20° and 32°.

The application of Hittorf's method to molten electrolytes by Lorenz and Fausti¹ is interesting. By the use of two porous clay cells, into which dipped carbon electrodes, they were able to show that in the electrolysis of a fused mixture of lead and potassium chlorides, the potassium migrates to the cathode and the lead to the anode, evidently as part of a complex anion.

Attention should be called to the papers of Stakelberg,² Burgess and Chapman³ and McBain⁴ on the determination of the relative velocities of complex ions which are partially dissociated into simpler ions.

3. *The Direct Determination of Ionic Velocities.*

The first direct determinations of the velocities of ions were made by Lodge⁵ in 1886. He dipped the two ends of a tube filled with dilute hydrochloric acid into vessels containing sulphuric acid and barium chloride, respectively, and passed a current through it from the salt solution to the acid. By noting the time, and the distance from the two ends of the tube of the point at which the barium and sulphate ions met, he was able to calculate their velocities. To prevent diffusion as much as possible, he substituted later, for the hydrochloric acid, a dilute solution of acetic acid in gelatin. In a second series of experiments he observed the actual progress of the chlorine ion by using silver sulphate as indicator and tracing the advance of the precipitate of silver chloride.

Whetham⁶ saw that Lodge's method had several objectionable features. The influence of the gelatin on the ionic velocities was entirely unknown, and no gelatin could be obtained so pure that it did not have a considerable conducting power of its own. In all methods based on the observation of the ad-

¹ Z. elek. Chem., **10**, 630 (1904).

² Z. physik. Chem., **23**, 493 (1897).

³ J. Chem. Soc., **85**, 1305 (1904).

⁴ Z. elek. Chem., **11**, 215, 961 (1905).

⁵ Brit. Assn. Rep., 1886, p. 389.

⁶ Phil. Trans. (A), 1893, p. 337.

vance of a precipitate, the precipitation of a part of the salt caused changes in concentration and, in aqueous solutions at least, mechanical disturbances. He therefore devised an apparatus in which the two solutions, which must have one ion in common while one of the other ions must possess a distinctive color, are held in a vertical tube, and the ionic velocity is determined by measuring the advance of the colored ion. To insure a uniform potential gradient, the two solutions must have about equal specific conductivities. Their densities must also be different in order to prevent mixing by diffusion. In a later series of experiments, Whetham¹ returns to the use of gelatin to prevent diffusion, and to precipitation methods to mark the advance of the ions. By making the quantity of indicator sufficiently small, the changes of concentration introduced by the last method become negligible. Lusanna² used Whetham's apparatus to study the effect of a magnetic field on ionic velocities.

Masson³ next took up the problem. He used Whetham's method, but placed his tube horizontally and used only colored solutions as indicators. He carefully studied the conditions which must govern the choice of an indicator solution. The colored ion must travel at a specifically slower rate than the ion whose advance it marks, and the indicator must be of such a nature that it will not react chemically with the gelatin or the salt under investigation, giving rise to new ions. Under such conditions, experiment shows that the boundary line between the colored and the colorless zones is very sharp, and Kohlrausch⁴ and Weber⁵ prove theoretically that there can be no mixture of the ions. In many cases, towards the end of the experiment, Masson noticed that cracks and flaws appeared in the gelatin, but this did not seem to affect the relative velocities of the moving boundaries.

A few years later, Steele⁶ devised a method which overcame many of the objectionable features of the older ones. The use

¹ Phil. Trans. (A), 1895, p. 607.

² Att. Ist. Ven., [7], 4, 1568 (1893).

³ Phil. Trans. (A), 192, 331 (1899).

⁴ Wied. Ann., 62, 209 (1897).

⁵ Sitz. Berl. Akad., 1897, p. 936.

⁶ Phil. Trans. (A), 198, 105 (1902).

of gelatin, as he notes, is impracticable, for the fall in potential is not uniform; the methods of Whetham and Masson are limited by the necessity of employing colored indicators, almost all of which give precipitates with the alkaline earths and the heavy metals. In his apparatus the solution under investigation is held in a vertical tube, between columns of gelatin containing the indicator in solution. The progress of the bounding layer can be easily followed, if the two solutions have slightly different refractive powers. The choice of indicators is thus largely increased. Measurements with salts like magnesium sulphate in both gelatin and water showed that the ionic velocities were affected by the gelatin, but with the alkali chlorides and bromides the velocities seem to be independent of the medium through which the ions travel.

Steele's values did not agree as well as could be desired with the transport numbers determined by Hittorf's method, and Abegg and Gauss¹ suggested that it might be due to endosmose. Modifying Steele's apparatus in such a way that they could measure the amount of solution forced through the gelatin and thus make the proper correction for it, they obtained, with potassium chloride, values agreeing very closely with those of Hittorf.

Denison² has extended this investigation to various other salts. He reaches the following conclusions:

1. In water, when correction is made for endosmose, the transport numbers for the simple sodium and potassium salts, determined in this way, agree with Hittorf's values.

2. For salts which form complex ions, or hydrolyze, the two sets of values do not agree but show parallelism.

3. Solid gelatin decreases the velocity of the cation. High concentration seems to have the same effect. Liquid gelatin does not influence the ionic velocities.

In a very recent paper, Denison and Steele³ describe an apparatus and method in which they have entirely discarded the use of gelatin. The solution under investigation is inclosed between layers of aqueous solutions of the indicators, usually

¹ *Z. physik. Chem.*, **40**, 737 (1902).

² *Ibid.*, **44**, 575 (1903).

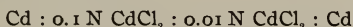
³ *Phil. Trans. (A)*, 1906, p. 449.

lithium chloride for the cation and sodium formate, acetate or benzene sulphonate for the anion. The lead cathode is covered with lead peroxide and surrounded with dilute acetic acid. The anode is of cadmium amalgam. A little lithium hydroxide in the anode chamber retains the hydrogen ions formed by the hydrolysis of the cadmium chloride. With this apparatus they determined the transport numbers for the chlorides of the alkalis and alkaline earths, the nitrate, sulphate, chlorate, bromate, bromide and iodide of potassium, the alkali hydroxides, and hydrochloric, nitric and sulphuric acids in 0.1 N and 0.02 N solutions, and have obtained values agreeing very satisfactorily with those obtained by Hittorf's method. They claim for their method just as great accuracy, and a very large saving in time and labor.

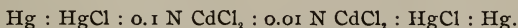
4. *Other Methods for Determining the Migration Velocities of Ions.*

Various other methods for determining migration velocities have from time to time been proposed.

Kummel,¹ who determined the transport numbers of the halides and sulphates of zinc and cadmium by the Hittorf method, also measured the electromotive forces of concentration elements of the type



and



As shown by Nernst,² from the ratio of the electromotive forces of two such elements, the transport numbers for the soluble salt can easily be calculated. Kummel obtained values for zinc and cadmium chlorides and cadmium sulphate that agreed very well with those found by the Hittorf method.

Kendrick³ determined the transport number of the anion of sulphuric acid, containing from 1.4 to 55 per cent of H_2SO_4 , by measuring the electromotive forces of 3 types of concentration elements:

¹ Wied. Ann., 64, 655 (1898).

² Z. physik. Chem., 4, 129 (1889).

³ Z. elek. Chem., 7, 52 (1900).

Pb : dil. H_2SO_4 : conc. H_2SO_4 : Pb ;

H_2 : dil. H_2SO_4 : conc. H_2SO_4 : H_2 ;

PbO_2 : dil. H_2SO_4 : conc. H_2SO_4 : PbO_2 .

McIntosh¹ shows that the ratio of the electromotive forces of concentration elements, with and without diffusion, is equal to the transport number, and by this means he determined the transference number of hydrogen. He used cells of the type—

H_2 : HCl : HgCl : HCl : H_2 —without diffusion ;

H_2 : HCl : HCl : H_2 —with diffusion.

The values obtained from duplicate experiments differ rather widely, and McIntosh concludes that the method is not applicable to gas cells, but it has been pointed out that the mean of his determinations does not differ more from the value calculated from Kohlrausch's conductivity measurements, than do the results of the different investigators using Hittorf's method.

When the solution of a salt, like copper sulphate, is electrolyzed, the process will be normal so long as the current density is kept below a certain point, but as soon as this critical point is passed, secondary processes set in and gas is evolved at the cathode. Weber² offered a possible explanation. At the critical density the copper ions, which, under a given electromotive force move with a fixed velocity, are just able to carry over all the positive electricity, and if this critical density is known, the absolute velocity of the ions can be calculated. Weber electrolyzed various solutions, gradually increasing the current density till a sudden rise in resistance gave evidence of polarization. This, he assumed, showed that the critical density had been reached. Experiments with copper and cadmium sulphates and zinc nitrate, gave results which agreed quite well with those of Kohlrausch.

Sheldon and Downing,³ using solutions of copper sulphate, increased the current density by gradually withdrawing the cathode, a cylinder of known diameter, from the solution. As soon as the critical density was reached, the copper ceased

¹ J. Phys. Chem., 2, 273 (1898).

² Z. physik. Chem., 4, 182 (1889).

³ Phys. Rev., 1, 51 (1894).

to be deposited in bright, metallic form, and the line of demarcation between the bright and the dark deposit was found to be quite sharp. They were thus able to determine the area of the cathode at the critical density, and from this the current density itself and the velocity of the copper ion.

5. Ionic Velocities in Non-aqueous Solvents.

Until within the last 3 years, very few determinations of ionic velocities had been made in solvents other than water. Hittorf, in his extensive investigation of transport numbers, electrolyzed a few solutions in ethyl and amyl alcohol. Lenz has recorded some measurements that he made with cadmium iodide in mixtures of water and alcohol.

Cattaneo¹ determined the effect of glycerol, methyl, ethyl and amyl alcohols, and mixtures of ethyl alcohol, chloroform and ether, on the transport number of the chlorine ion in hydrochloric acid. He found in all cases that the influence of the solvent was very slight. Campetti² measured the transport numbers for lithium chloride and silver nitrate in ethyl alcohol. Whetham determined directly the velocity of the cobalt ion in alcoholic solutions of cobalt chloride and nitrate. Mather worked with silver nitrate in mixtures of ethyl alcohol and water.

Schlundt³ carried out some experiments with silver nitrate in pyridine and acetonitrile. Silver nitrate has a great "affinity" for these two liquids, and crystallizes from pyridine with 2 and 3 molecules of the solvent. As Schlundt expected, the relative velocity of the silver ion increases with the dilution. This is analogous to the phenomena observed in aqueous solution, with those salts which come out of solution with water of crystallization; the transport number of the cation almost always increases with the dilution.

Roth⁴ gives some unpublished determinations of transport numbers made by Hornbostel and Goldberger, in mixtures of ethyl alcohol and water, containing from 10 to 40 per cent of

¹ Rend. Acc. Lincei [5], 5, 207 (2 sem., 1897); [5], 6, 279 (1 sem., 1898).

² Il Nuovo Cimento, 35, 225 (1894). Ref., Z. physik. Chem., 16, 165 (1895).

³ J. Phys. Chem., 6, 159 (1902).

⁴ Z. physik. Chem., 42, 219 (1903).

alcohol. Eisenstein¹ also worked along this line. From sodium chloride, the transport number of the chlorine ion increases with the amount of alcohol, but is unaffected by dilution. Goldberger's results with barium chloride are given below: v = the number of liters of solution containing a gram-molecular weight of the salt; a = the transport number of the anion:

v .	Percentage of Alcohol.					
	0 per cent. a .	10 per cent. a .	20 per cent. a .	25 per cent. a .	30 per cent. a .	40 per cent. a .
30	0.543	0.531	0.540	0.549		0.536
60	0.548	0.536	0.543	0.551	0.545	0.536
90	0.553	0.545	0.547	0.550		0.536
120	0.554	0.546				0.536

The addition of small quantities of alcohol to the aqueous solution produces a lowering of the transport number, but as the proportion of alcohol is increased the relative velocity of the chlorine ion also increases, and reaches a maximum value in the mixture containing 25 per cent of alcohol. A further addition of alcohol produces a steady decrease. The transport number also increases with the dilution.

The first systematic study of ionic velocities in non-aqueous solvents was made by Carrara.² He used three pieces of apparatus, two of which had been devised by earlier investigators, Hittorf and Loeb and Nernst, while the third, he claims, is a new form, although it is very similar to that of Jones and Mather. He determined the transport numbers for some 20 salts of copper, cadmium and lithium, in methyl alcohol and, comparing them with the corresponding values for aqueous solutions, reached the conclusion that the relative velocities of the ions of an electrolyte tend toward the same value, independent of the solvent.

Dempwolf,³ shortly afterwards, also determined the transport numbers for a large number of salts in methyl alcohol, and found that the oxymethyl ion, OCH_3 , of sodium methylate, has a velocity about equal to that of the chlorine ion.

¹ Dissertation, Berlin, 1902.

² Gazz. chim. ital., **33**, I., 241 (1903).

³ Physik. Z., **5**, 637 (1904).

Jones and Bassett,¹ with the same apparatus that has been used in the present investigation, measured the relative velocity of the anion of silver nitrate at 0° and 25° in water, methyl and ethyl alcohol, and mixtures of water and methyl alcohol. They draw the following conclusions from their work :

“The difference in the relative velocities observed in the pure solvents at 0° and 25°, become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the case of mixed solvents.

“The relative velocities are largely dependent on the nature of the solvent.

“In mixed solvents the relative velocities are dependent on both the temperature and the composition of the mixture.”

One of the most interesting investigations ever carried out in this field is that of Franklin and Cady,² on the determination of transport numbers of various salts in liquid ammonia. With considerable ingenuity they so modified Steele's apparatus that they were able to use it, satisfactorily, with such a low-boiling solvent as ammonia. The lower part of the tube was closed by a thread of mercury. In determinations of the velocities of cations, this mercury thread served as anode, and the mercury ions thus formed as the indicators. For anions, picric acid was generally employed as indicator. They found that for sodium and potassium nitrates, and sodium chloride and bromide, the ionic velocities are independent of the concentration. As was to be expected from the dielectric constant and association factor of liquid ammonia, the results of their work showed that the unusually high conductivities of solutions in this liquid, observed by Cady,³ were due, not to a large dissociation, but to the high velocities of the ions in this medium. From their determinations of transport numbers and Cady's conductivity measurements, they demonstrate that the conductivity of completely dissociated electrolytes in liquid

¹ THIS JOURNAL, 32, 409 (1904).

² J. Am. Chem. Soc., 26, 499 (1904).

³ J. Phys. Chem., 1, 707 (1897).

ammonia is 2.5 to 3 times as high as the corresponding values in water.

Equally interesting is the very recent work of Steele, McIntosh and Archibald¹ on the properties of the liquid halogen acids. They find that such compounds as ether, acetone, substituted ammonium salts and ketones, in general, dissolved in liquid hydrobromic acid, conduct the current very well. After satisfying themselves, by measuring the amount of hydrogen liberated during electrolysis, that these solutions obey Faraday's law, they determined the transport number of the cation at two dilutions. They conclude that liquid hydrobromic acid forms addition products with the solute, and that these dissociate into complex cations and simple bromine anions.

PART II.

EXPERIMENTAL.

Object of This Investigation.

This work is a direct continuation of the investigation carried out in this university two years ago by Jones and Bassett.² They wished, if possible, to trace a connection between the phenomena of minimum conductivity, first observed by Zelinsky and Krapivin³ and later extensively studied by Jones and Lindsay,⁴ which solutions in certain mixtures of alcohol and water exhibit. Jones⁵ and his students have extended the investigation of this problem to mixtures of other solvents, including acetone, and have obtained interesting results. It was, therefore, thought desirable to extend also the work of Jones and Bassett. The conductivity of silver nitrate and the transport number of its anion in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone, have been determined at two temperatures, 0° and 25°. In their determination of transport numbers, Jones and Bassett worked with 0.1 N solutions, but, owing to the limited solubility of silver nitrate in acetone, and to the desira-

¹ Phil. Trans. (A), 1905, p. 99.

² THIS JOURNAL, 32, 409 (1904).

³ Z. physik. Chem., 21, 35 (1896).

⁴ THIS JOURNAL, 28, 329 (1902).

⁵ *Ibid.*, 32, 521 (1904); 34, 481 (1905).

bility of having comparable values throughout, all measurements in this work have been made with 0.02 N solutions.

Solvents.

Water.—The water used in preparing the solutions was purified essentially by the method of Jones and Mackay.¹ Ordinary distilled water was twice redistilled from an acidified solution of potassium bichromate, and the steam from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about 1.0×10^{-6} .

Methyl Alcohol.—The purest obtainable product was boiled 1 to 2 days with lime, distilled and allowed to stand over anhydrous copper sulphate till needed. All distillations were made through a Singer fractionating head and a block-tin condenser, and the liquid was protected during distillation from the moisture in the air by means of a soda lime U-tube. To prevent any possibility of soda lime dust being drawn back into the liquid, the end of the tube nearest the bottle was covered with filter paper. The first and last portions of the distillate were always discarded. The mean conductivity at 0° = 0.8×10^{-6} .

Ethyl Alcohol.—The best commercial article was treated in the same manner as the methyl alcohol. Its conductivity at 0° was about 2.0×10^{-7} .

Acetone.—The acetone was allowed to stand over fused calcium chloride before using. Conductivity at 0° = 1.0×10^{-6} .

Mixed Solvents.—The mixture obtained by adding n cc. of Solvent *A* to $100-n$ cc. of Solvent *B* was designated as an “ n per cent *A*—($100-n$) per cent *B* mixture.” This method of preparing mixed solvents was deemed preferable to the more common method of diluting n cc. of Solvent *A* to 100 cc. with Solvent *B*. In the latter case it is always necessary to state which solvent is used as diluent, and the mixture must always be allowed to cool down to the temperature of the unmixed solvents before the final dilution to the mark on the measuring flask can be effected.

¹ THIS JOURNAL, 19, 83 (1897).

I. Conductivity.

Apparatus.—In making conductivity measurements, the usual Kohlrausch method, with Wheatstone bridge, induction coil and telephone receiver, was used. The bridge wire was of "manganin." The resistance coils were made by Leeds, of Philadelphia, and were calibrated to within 0.04 of 1 per cent.

The conductivity cells were of the type devised by Jones and Bingham¹ for use with volatile solvents, which, like acetone, attack rubber and wax. They differ from the simple Arrhenius cells in that the cup is closed by a ground glass stopper, into which are sealed with glass the tubes that carry the electrodes.

The electrodes were carefully cleansed with chromic acid and covered with platinum black, by electrolyzing a dilute solution of platinic chloride. All absorbed chlorine was removed with sodium hydroxide and the plates were washed with dilute hydrochloric acid and distilled water, dried and heated to redness in the flame of a blast-lamp. Electrodes thus treated gave a good tone minimum, did not appreciably absorb salts from their solutions and showed no tendency to cause the rapid oxidation of alcohol to acetic acid. When not in use the cells were filled with distilled water. Solutions were never allowed to stand in them longer than was necessary.

The 0° bath was of the form commonly used in this laboratory. A tin pail was filled with finely crushed ice and water and the cells were then packed into the ice as tightly as possible. The pail was placed into a larger, indurated filter bucket and the intervening space filled with finely crushed ice and water. Such a bath will maintain a temperature to within 0°.1 of 0° for hours. The 25° bath was a galvanized iron tub, lined on the outside with asbestos. The water in it was kept at a uniform temperature by means of a stirrer driven by a small hot-air motor, and could easily be kept to within 0°.1 of any desired temperature. The thermometers were graduated to 0°.1 and standardized. The burettes and measuring flasks

¹ THIS JOURNAL, 34, 481 (1905).

were all carefully calibrated by the method of Morse and Blalock.¹

Preparation of Solutions.—The silver nitrate used in this work was obtained from Kahlbaum, and was perfectly neutral. It was finely pulverized, dried for several hours at 100°–105° and kept in a desiccator in the dark. Somewhat more of the salt than was necessary to prepare a 0.02 N solution was weighed into the solvent, and the exact concentration was determined by titration with a 0.04 N solution of ammonium sulphocyanate, with ferric ammonium sulphate as indicator. The sulphocyanate solution was standardized against a 0.04 N solution of silver nitrate, and weighed quantities of thoroughly dried potassium chloride, which had been especially purified in this laboratory for use in conductivity work. The solution whose conductivity was to be measured was then made exactly 0.02 N by the addition of the proper amount of solvent. From this mother-solution the other solutions were prepared by successive dilution. The N/800 and N/1200 solutions were prepared from the N/400.

Conductivity Measurements.—In measuring the conductivity of a solution, readings were always made with three different resistances, and the values given are the mean. Before using, the cells and electrodes were carefully dried and rinsed out with the solution whose conductivity was to be measured. The cell constants were determined with 0.02 N and 0.004 N solutions of pure potassium chloride. The molecular conductivity of the former was taken as 129.7 at 25°.

In the following tables, under v is given the concentration, expressed in number of liters of the solution containing a gram-molecular weight of the salt; under μ_v 0°, the molecular conductivity at 0°; and under μ_v 25°, the molecular conductivity at 25°.

The temperature coefficients are obtained by dividing the increase in conductivity per degree by the conductivity at 0°.

The values for the molecular conductivities in water and methyl and ethyl alcohols are obtained, by interpolation, from

¹ THIS JOURNAL, 16, 479 (1894).

the measurements of Jones and Bassett, and the temperature coefficients are calculated from those interpolated values.

Table I.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	38.97	78.79
100	40.91	81.82
200	42.36	85.70
400	41.65	85.00
800	43.24	88.24
1200	45.01	91.71

Conductivity of solvent at 0° = 1.15×10^{-6} .

Table II.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 15°.
50	31.31	62.97
100	31.72	64.34
200	33.00	67.69
400	33.74	68.50
800	34.32	71.12
1200	34.57	70.60

Conductivity of solvent at 0° = 1.66×10^{-6} .

Table III.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	30.79	53.04
100	34.59	60.05
200	36.49	63.81
400	38.75	68.34
800	40.35	70.63
1200	40.26	71.28

Conductivity of solvent at 0° = 2.06×10^{-6} .

Table IV.—Molecular Conductivity of Silver Nitrate in Acetone.

<i>v.</i>	μ_v 0°.	μ_v 25°.
125	7.93	10.08
200	8.18	10.36
400	8.58	11.57
800	9.64	12.08
1200	10.54	13.11

Conductivity of solvent at 0° = 1.0×10^{-6} .

Table V.—Molecular Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents at 0°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	63.11	38.97	31.31	30.79	. .
100	63.71	40.91	31.72	34.59	. .
200	66.51	42.36	33.00	36.49	8.18
400	70.19	41.65	33.74	38.75	8.58
800	70.94	43.24	34.32	40.35	9.64
1200	70.65	45.01	34.57	40.26	10.54

Table VI.—Molecular Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents at 25°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	111.62	78.79	62.97	53.04	. .
100	116.82	81.82	64.34	60.05	. .
200	121.16	85.70	67.69	63.81	10.36
400	125.27	85.00	68.50	68.34	11.57
800	125.73	88.24	71.12	70.63	12.08
1200	125.43	91.71	70.60	71.28	13.11

Table VII.—Temperature Coefficients of Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents, 0°–25°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0307	0.0409	0.0404	0.0289	. .
100	0.0334	0.0400	0.0411	0.0294	. .
200	0.0329	0.0409	0.0430	0.0299	0.0107
400	0.0314	0.0416	0.0424	0.0305	0.0139
800	0.0309	0.0416	0.0429	0.0300	0.0101
1200	0.0310	0.0415	0.0417	0.0308	0.0097

The values in Tables I. to VI. are plotted as curves in Figs. I. and II., the abscissae representing the different percentages of acetone, and the ordinates the molecular conductivities. It

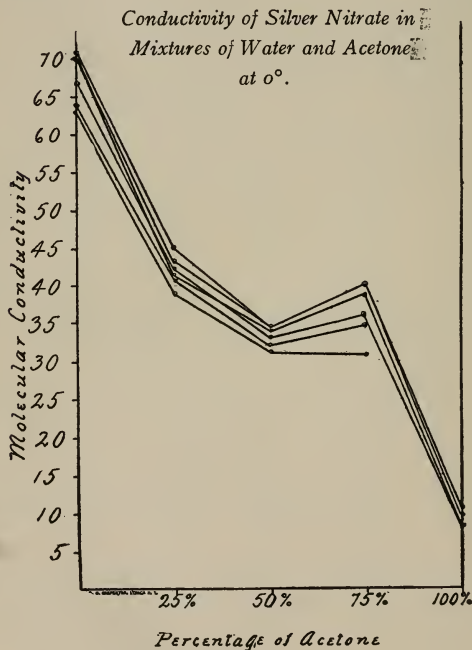


Fig. I.

will be seen that at 0°, for all dilutions but the lowest investigated, 0.02 N, there is a pronounced point of inflection that appears in the 75 per cent acetone mixture. At 25° it has al-

most disappeared, but still manifests itself at the higher dilutions. The curves are almost identical in form with those obtained by Jones and Bingham¹ for calcium nitrate, in mixtures of the same solvents.

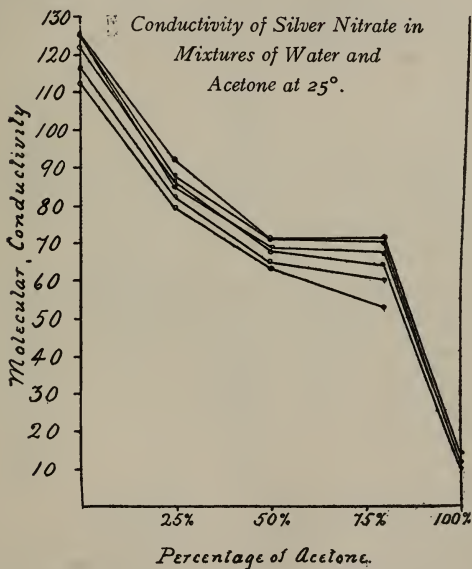


Fig. II.

Table VII. shows that the temperature coefficients increase with the proportion of acetone up to the 50 per cent mixture, but a further increase in the proportion of acetone produces a

¹ THIS JOURNAL, 34, 481 (1905).

rapid fall in the values for the temperature coefficients. With increase in concentration, the maximum value tends to shift to the 25 per cent acetone mixture. These results are also almost identical with those obtained by Jones and Bingham with calcium nitrate.

Table VIII.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	32.39	45.69
100	38.01	54.09
200	44.94	64.40
400	47.09	67.72
800	50.45	72.85
1200	51.66	74.88

Conductivity of solvent at 0° = 7.4×10^{-7} .

Table IX.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	24.06	35.24
100	29.04	42.39
200	32.17	47.29
400	35.93	53.04
800	39.22	58.10
1200	40.06	59.68

Conductivity of solvent at 0° = 3.1×10^{-7} .

Table X.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent. Methyl Alcohol—75 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	17.45	26.54
100	20.78	31.89
200	23.40	36.41
400	26.45	41.32
800	28.38	44.71
1200	28.91	46.03

Conductivity of solvent at 0° = 3.8×10^{-7} .

Table XI.—Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols and Mixtures of These Solvents at 0°.

v.	Percentage of Ethyl Alcohol.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	41.10	32.39	24.06	17.45	11.79
100	46.73	38.01	29.04	20.78	13.61
200	52.49	44.94	32.17	23.40	15.61
400	57.89	47.09	35.93	26.45	17.64
800	. .	50.45	39.22	28.38	. .
1200	. .	51.66	40.06	28.91	. .

Table XII.—Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols, and Mixtures of These Solvents at 25°.

v.	Percentage of ethyl alcohol.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	55.80	45.69	35.24	26.54	17.75
100	64.80	54.09	42.39	31.89	21.05
200	72.81	64.40	47.29	36.41	24.52
400	82.18	67.72	53.04	41.32	27.50
800	. .	72.85	58.10	44.71	. .
1200	. .	74.88	59.68	46.03	

Table XIII.—Temperature Coefficients of Conductivity of Silver Nitrate in Methyl and Ethyl Alcohol and Mixtures of These Solvents, 0°–25°.

v.	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0164	0.0186	0.0208	0.0202
100	0.0155	0.0169	0.0184	0.0214	0.0189
200	0.0155	0.0173	0.0188	0.0222	0.0203
400	0.0168	0.0175	0.0190	0.0225	0.0224
800	. .	0.0178	0.0192	0.0230	. .
1200	. .	0.0180	0.0196	0.0237	. .

Tables VIII. to XII. (Figs. III. and IV.) show that there is no trace of either a maximum or minimum, the curves being

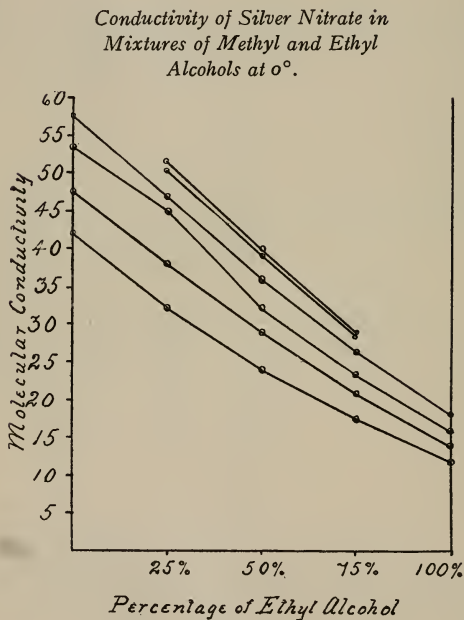


Fig. III.

straight lines to within the limits of experimental error. The temperature coefficients (Table XIII.) increase regularly with

the proportion of ethyl alcohol up to the 75 per cent mixture, and then remain practically constant, showing a slight tendency to drop.

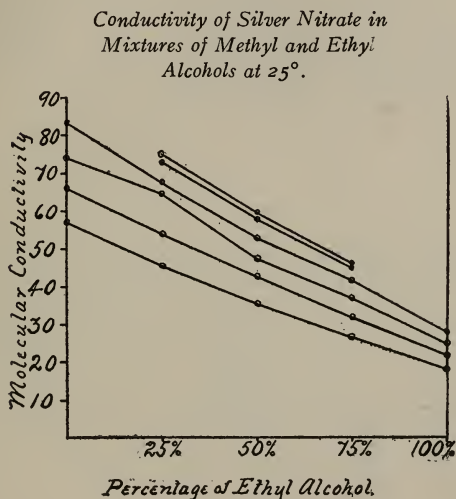


Fig. IV.

Table XIV.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	40.45	53.81
100	46.36	64.24
200	55.60	73.65
400	63.98	83.08
800	65.62	92.69
1200	71.85	96.70

Conductivity of solvent at 0° = 1.3×10^{-6} .

Table XV.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	38.46	45.94
100	48.31	61.69
200	58.22	68.61
400	67.87	83.88
800	77.83	100.90
1200	81.57	100.40

Conductivity of solvent at 0° = 1.36×10^{-6} .

Table XVI.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	25.49	28.40
100	33.67	37.78
200	42.42	47.00
400	51.50	59.87
800	63.19	75.12
1200	66.71	78.19

Table XVII.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	41.10	40.45	38.46	25.49	. .
100	46.73	46.36	48.31	33.67	. .
200	52.49	55.60	58.22	42.42	8.18
400	57.89	63.98	67.87	51.50	8.58
800	. .	65.62	77.83	63.19	9.64
1200	. .	71.85	81.57	66.71	10.54

Table XVIII.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 25°.

v.	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	55.80	53.81	45.94	28.40	. .
100	64.80	64.24	61.69	37.78	. .
200	72.81	73.65	68.61	47.00	10.36
400	72.18	83.08	83.88	59.87	11.57
800	. .	92.69	100.90	75.12	12.08
1200	. .	96.70	100.40	78.19	13.11

Table XIX.—Temperature Coefficients of Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.

v.	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0132	0.0078	0.0046	. .
100	0.0155	0.0154	0.0119	0.0049	. .
200	0.0155	0.0130	0.0071	0.0068	0.0107
400	0.0168	0.0119	0.0119	0.0065	0.0139
800	. .	0.0165	0.0119	0.0076	0.0101
1200	. .	0.0138	0.0092	0.0069	0.0097

A study of Tables XIV. to XVIII. (Figs. V. and VI.) shows that at 0°, at the higher dilutions, silver nitrate in mixtures of methyl alcohol and acetone gives a maximum that almost disappears at 25°, although still evident in the more dilute solutions. The maximum appears in the 50 per cent

mixture. Here again the results are very similar to those found for calcium nitrate by Jones and Bingham, although silver nitrate does not, like the calcium salt, show, within the

*Conductivity of Silver Nitrate in
Mixtures of Methyl Alcohol and
Acetone at 0°.*

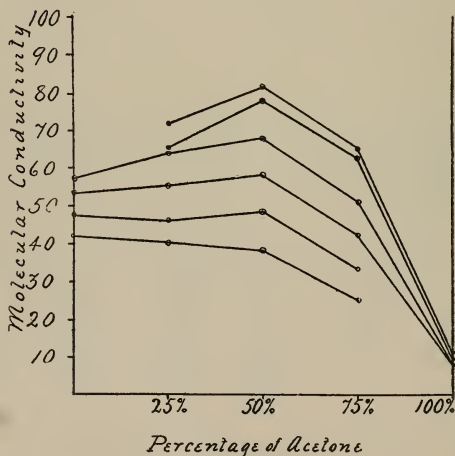


Fig. V.

limits of the dilutions investigated, any maximum in the 25 per cent acetone mixture.

The temperature coefficients (Table XIX.) exhibit a pro-

nounced maximum in the 75 per cent acetone mixture. This applies equally well to calcium nitrate.

*Conductivity of Silver Nitrate in
Mixtures of Methyl Alcohol and
Acetone at 25°.*

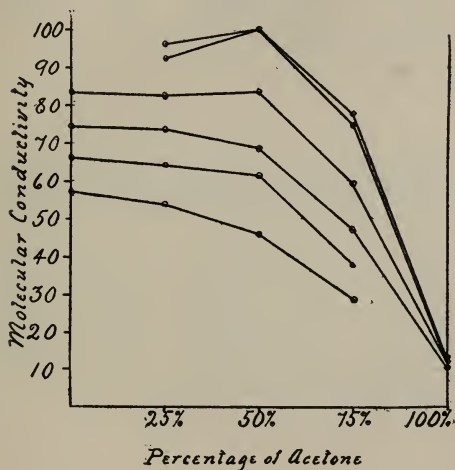


Fig. VI.

Table XX.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	15.86	22.39
100	19.90	28.38
200	25.06	33.64
400	27.40	39.82
800	31.51	46.30
1200	32.85	49.04

Conductivity of solvent at 0° = 2.4×10^{-7} .

Table XXI.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	16.91	21.42
100	22.13	28.12
200	25.72	33.64
400	33.55	43.49
800	40.51	53.51
1200	43.90	58.69

Conductivity of solvent at 0° = 4.6×10^{-7} .

Table XXII.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Ethyl Alcohol—75 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	13.38	16.36
100	17.42	23.06
200	22.20	27.60
400	29.80	.
800	37.84	45.80
1200	43.76	55.33

Conductivity of solvent at 0° = 4.4×10^{-7} .

Table XXIII.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	11.79	15.86	16.91	13.38	. .
100	13.61	19.90	22.13	17.42	. .
200	15.61	25.06	25.72	22.20	8.18
400	17.64	27.40	33.55	29.80	8.58
800	. .	31.51	40.51	37.84	9.64
1200	. .	32.85	43.90	43.76	10.54

Table XXIV.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 25°.

v.	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	17.75	22.39	21.42	16.36	. .
100	21.05	28.38	28.12	23.06	.
200	24.52	33.64	33.64	27.60	10.36
400	27.50	39.82	43.49	. .	11.57
800	. .	46.30	53.51	45.80	12.08
1200	. .	49.04	58.69	55.33	13.11

Table XXV.—Temperature Coefficients of Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.

v.	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0202	0.0165	0.0107	0.0089	. .
100	0.0189	0.0170	0.0108	0.0130	. .
200	0.0203	0.0137	0.0123	0.0097	0.0107
400	0.0224	0.0181	0.0118	. .	0.0139
800	. .	0.0188	0.0128	0.0084	0.0101
1200	. .	0.0197	0.0134	0.0106	0.0097

The similarity of the curves (Figs. VII. and VIII.) plotted from the values given in Tables XX. to XXIV., to the corresponding curves obtained by Jones and Bingham for calcium nitrate, is even more striking than in the case of the methyl alcohol and acetone mixtures. A pronounced minimum manifests itself at both 0° and 25°, appearing in the 25 per cent acetone mixture in the more concentrated solutions, and shifting, with increase in dilution, through the 50 per cent to the 75 per cent mixture.

As with calcium nitrate, the temperature coefficients (Table XXV.) show a minimum in the 75 per cent mixture.

In view of the great similarity in conductivity phenomena

exhibited by silver and calcium nitrates, in mixtures of water and of methyl and ethyl alcohols with acetone, it is interesting to know whether this is also true of solutions of the two salts in mixtures of water with the alcohols. By comparing the

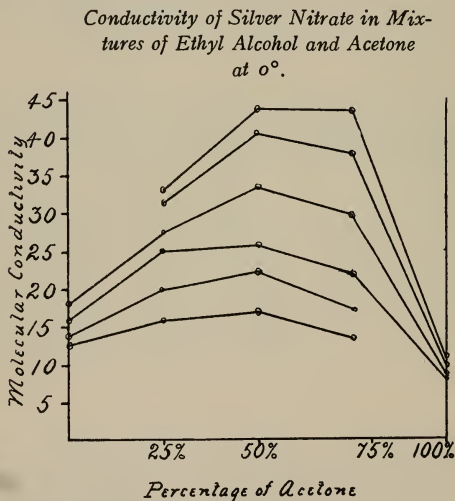


Fig. VII.

values for calcium nitrate in these mixtures, obtained by Jones and Carroll,¹ with the corresponding values for the silver salt which had been obtained by Jones and Bassett, it is seen

¹ THIS JOURNAL, 32, 521 (1904).

that in mixtures of ethyl alcohol with water the conductivity curves for both salts are of the same form, showing no marked minimum, but exhibiting a tendency towards one in the 75 per

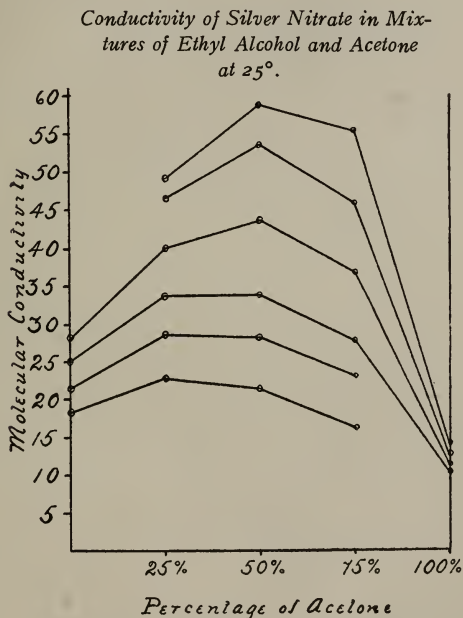


Fig. VIII.

cent alcohol mixture. In mixtures of methyl alcohol with water, however, while silver nitrate gives a very marked minimum in the 50 per cent mixture, the calcium salt does not.

Jones and Carroll did not work with dilutions greater than $N/256$, and it is quite possible that more dilute solutions would show a minimum.

II. Migration Velocity.

Apparatus.—The apparatus used in this investigation for the determination of the relative velocities of the ions of silver nitrate was devised by Jones and Bassett.¹ It is a modification of the form Mather² devised while working with Jones. The two outer limbs are 20 cm. long and 2 cm. in diameter and are connected 3 cm. below the stoppers, by a U-tube 1.5 cm. in diameter. Each arm of the U-tube is 10 cm. long, and at the center of it is a stop-cock of large bore (1 cm.). Into the electrodes, made of disks of pure silver, is riveted a short piece of stout platinum wire, which is then sealed into thick-walled glass tubes of 2 mm. bore. The exposed end of the platinum wire on the under side of the electrode is covered with fusion glass. The tubes carrying the electrodes are forced through holes bored into the ground-glass stoppers, which close the upper ends of the limbs of the apparatus. They are held firmly in place by pieces of rubber tubing. To prevent the solution from coming in contact with this rubber tubing, rings or flanges are blown on the glass tubes at the place where they enter the stopper, and are ground with carborundum to fit tightly into the holes in the stopper. To the limbs of the apparatus, just below the stoppers, are attached small, graduated tubes, 3 mm. in diameter, extending outward and upward. It was found, especially with alcohol and acetone solutions, that when the apparatus was placed in the 25° bath, a small quantity of gas always collected under the stopper and forced out some of the liquid through the side tubes. To prevent loss of solution from this source, the capacity of the side tubes was increased by attaching to them, by means of short pieces of thick rubber tubing, glass tubes of the same diameter with bulbs blown in them. An ordinary straight calcium chloride tube of small size answers the purpose very well.

¹ THIS JOURNAL, 32, 429 (1904).

² *Ibid.*, 26, 473 (1901).

Electrical connection is made with the electrodes through the platinum wires riveted into them by filling the tubes which carry them with mercury.

The advantages of this form of apparatus are evident. It is easily made and handled. It is perfectly symmetrical, so that either side can be used as cathode chamber. All danger of diffusion is done away with and no membrane is necessary. The stoppers being at the top, there can be no leakage, its comparatively large capacity, about 130 cc., which may be very accurately determined, making it possible to work with large quantities of solution. By means of the small side tubes the liquid in both arms can be very accurately leveled and, finally, the stop-cock at the center of the U-tube makes it possible to separate completely the cathode and anode solutions, and to rinse out the two sides as thoroughly as may be desired. By making the bore of the stop-cock sufficiently large, the resistance offered to the current is not materially increased.

The constant temperature bath was also constructed on the same general principles as that of Jones and Bassett.¹ A wooden box, 24 inches long, 14 inches wide and 10 inches deep, is lined to within half an inch of the top with thick, galvanized iron. On one side, 1.5 inches from the top, is a heavy, movable shelf, which serves to hold the voltameters. On the opposite side are wire hooks so arranged that, when the migration velocity apparatus is hung on them the bottom of the stoppers is level with the shelf. A section of the wooden bottom, 14 inches square, is removed and the contents of the bath can thus be heated by means of a small flame. The box is filled to the level of the shelf with water, which is kept at a uniform temperature by a small stirrer, driven by a hot-air motor. The bath proved very effective, being easily kept to within 0°.1 of the desired temperature. For measurements at 0°, the bath was filled with finely crushed ice, moistened with water, and the pieces of apparatus packed into the ice as tightly as possible. With a bath of these dimensions, 3 determinations can easily be carried out simultaneously.

The current used was always measured by means of a silver

¹ THIS JOURNAL, 32, 430 (1904).

voltameter. On a copper disk at the bottom of a weighing bottle was placed a platinum crucible, nearly filled with a 0.1 N solution of silver nitrate. Into this solution the anode, a bar of pure silver, was dipped by forcing it through a rubber stopper which served to close the weighing bottle. The anode was wrapped in a linen bag to prevent any detached particles from falling into the crucible. Connection with the circuit was established through copper wires soldered to the disk and the silver anode.

The binding posts on the bath, used to make electrical connection with the migration velocity apparatus and the voltameters, were placed on blocks of hard rubber, and in all the wiring special precautions were taken to prevent any leakage of current. Only heavily insulated copper wire was used, and at no point was it allowed to touch the bath, being held in position by porcelain insulators. Wherever two wires were placed near each other, they were further insulated by slipping a piece of rubber tubing over them.

Migration Velocity Measurements.—All the solutions used in this work were made up approximately 0.02 N, their exact concentration being determined by titration with a solution of ammonium sulphocyanate, which had been standardized in the manner described under "conductivity measurements."

Before every experiment the crucibles of the voltameters were treated with boiling nitric acid, fused acid potassium sulphate and boiling water. They were then heated to redness and weighed. After such treatment the silver was always deposited in a very adherent form, and could easily be washed without danger of loss. At the conclusion of the experiment the crucibles were rinsed out, allowed to stand over night full of distilled water, again rinsed out, dried from 30–60 minutes at 110°–115° and cooled in a desiccator.

To determine the capacity of each arm of the migration velocity apparatus, the stoppers were placed in position, the stop-cock closed, and each side filled from a burette to the zero mark on the small side tubes. To effect this, the burette was provided with a long, slender false tip, which could reach to the bottom of the side tubes.

To fill the apparatus with the solution to be electrolyzed, both stoppers were placed in position and one of the side tubes closed with a Bunsen valve. The other was connected by a piece of rubber tubing to a glass tube passing through a two-holed stopper to the bottom of the flask containing the solution. Through the other hole of the stopper passed a short glass tube connected with a soda lime U-tube. The end of the soda lime tube nearest the flask was covered with filter paper. By blowing through this tube, the solution could be forced over into the apparatus. The side tube was closed with a second Bunsen valve, the apparatus placed in the bath, and the current passed through the solution. The electrolysis was allowed to proceed till a sufficient amount of silver had been deposited in the voltameter, usually from 0.5–0.1 gram. The liquid in both arms was then carefully leveled, the stop-cock turned, and the cathode and anode solutions filtered through glass wool into 250 cc. measuring flasks and diluted nearly to the mark with the water used to rinse out the apparatus. After standing several hours, usually over night, the solutions were diluted to exactly 250 cc., and 100 cc. portions were titrated for their silver contents. Knowing the concentration of the solution before the electrolysis, the capacity of each arm of the apparatus, the amount of silver in the cathode solution after the electrolysis, and the amount of silver deposited in the voltameter, the relative migration velocity a of the anion was calculated from the equation

$$a = \frac{\text{loss of silver on cathode side}}{\text{silver deposited in voltameter}}.$$

To determine whether there had been any loss of silver by deposition of the peroxide on the anode, or from impurities in the electrodes, the anode solutions were also titrated.

Two different currents were used : one of 72 volts, furnished by a battery of storage cells, and one of 110 volts, supplied from the University power house. The current of lower voltage gave uniformly better results. The silver was usually deposited in beautiful needles on the cathode but, in some cases, especially where the current density was relatively high, the

deposit was more or less dark and of a spongy character. A thin covering of silver peroxide was generally deposited on the anode, and the analysis of the solution after the electrolysis usually showed that there had been a loss of from 0.5–1.0 per cent of silver. Some of the solutions offered a very great resistance to the passage of the current, and the electrolysis had to be continued from 12–20 hours. As it was impracticable, when working at 25° , to let the electrolysis proceed over night, it was attempted to use the city current of 220 volts which, however, was subject to rapid and irregular fluctuations all the way from 180–250 volts, but all such attempts were unsuccessful. The silver came down on the cathode in a very unsatisfactory form; there was a considerable deposition of peroxide on the anode, with a loss of silver of from 5–10 per cent, and the values obtained for the transport numbers from duplicate experiments did not show satisfactory agreement.

The acetone and alcohol solutions attacked, to a slight extent, the grease used to lubricate the stoppers and stop-cock, as was shown by the faint turbidity produced on diluting with water, but this source of error was not sufficient to affect the results materially.

The current never exceeded 0.005 ampere, and in some cases was as low as 0.001 ampere.

In the following tables, m_1 = the concentration of the solution before the electrolysis, expressed in fractions of gram-molecular weights of the salt contained in one liter of the solution; m_2 = concentration of the cathode solution after electrolysis; v = weight of silver in grams, deposited in the voltameter; and a = the transport number of the anion.

Table XXVI.—Relative Velocity of the Anion of Silver Nitrate in Water at 0° .

m_1 .	m_2 .	v .	a .
0.01999	0.01499	0.0657	0.563
0.01999	0.01464	0.0679	0.562
0.01984	0.01194	0.1014	0.557
0.01999	0.01488	0.0647	0.541

Table XXVII.—Relative Velocity of the Anion of Silver Nitrate in Water at 0° , as Determined by Different Observers.

m_1 .	a .	
0.1	0.5409	(Mather)
0.102	0.5628	(Jones and Bassett)
0.025	0.5377	(Mather)
0.025	0.5383	(Loeb and Nernst)
0.02	0.555	(Jones and Rouiller)

The value that we obtained is higher than that given by Mather, and by Loeb and Nernst for solutions of about the same concentration, while Jones and Bassett found, with a 0.1 N solution, a value higher than our own for the more dilute solution.

Table XXVIII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02036	0.01545	0.0671	0.546
0.02036	0.01573	0.0607	0.544
0.02030	0.01540	0.0628	0.549
0.02030	0.01551	0.0656	0.532
0.02030	0.01496	0.0703	0.541

Table XXIX.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02079	0.01784	0.0399	0.541
0.02079	0.01741	0.0418	0.576
0.02069	0.01753	0.0420	0.551
0.02069	0.01723	0.0437	0.564

Table XXX.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02016	0.01379	0.0848	0.514
0.02016	0.01561	0.0763	0.536

Table XXXI.—*Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.*

m_1 .	m_2 .	v .	a .
0.02001	0.01483	0.0632	0.562
0.02001	0.01521	0.0629	0.559
0.02001	0.01479	0.0662	0.563

Table XXXII.—*Relative Velocity of the Anion of Silver Nitrate in Water at 25°.*

m_1 .	m_2 .	v .	a .
0.01999	0.01073	0.1211	0.544
0.01999	0.01128	0.1202	0.536
0.01999	0.01070	0.1155	0.543
0.02003	0.01069	0.1194	0.539

For the sake of comparison, the following table has been prepared :

Table XXXIII.—*Relative Velocity of the Anion of Silver Nitrate in Water at Various Temperatures, as Determined by Different Observers.*

t .	m .	a .	
11°.2	2.22	0.468	(Hittorf)
19°	2.02	0.478	"
18°.4	1.09	0.495	"
18°.8	0.87	0.510	"
75°-97°	0.49-0.64 ¹	0.513	(Bein)
9°.6-19°.2	0.39-0.024	0.5256	(Hittorf)
	0.18-0.27	0.520	(Wiedemann ²)
13°-15°	0.17 ¹	0.525	(Bein)
20°	0.104	0.528	(Loeb and Nernst)
29°.1	0.1	0.5317	(Mather)
47°.4-47°.7	0.1	0.5279	"
25°	0.1	0.5285	(Jones and Bassett)
26°	0.0521	0.524	(Loeb and Nernst)
18°-19°	0.033-0.0047	0.529	(Jahn)
26°	0.025	0.5223	(Loeb and Nernst)
45°	0.025	0.5246	(Mather)
25°	0.020	0.540	(Jones and Rouiller)
15°	0.01891	0.531	(Kistiakowsky)
26°	0.0105	0.5235	(Loeb and Nernst)

¹ Only a rough approximation; Bein expresses the concentration of his solutions in terms of percentages of silver, but does not give the specific gravity of the solutions.

² Wiedemann does not give the temperature at which he worked.

The value for the transport number, as this table shows, increases with the dilution. The value which we obtained is considerably higher than that found by other observers.

Table XXXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02002	0.01449	0.0753	0.522
0.02002	0.01436	0.0788	0.531
0.02002	0.01356	0.0817	0.534

Table XXXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02080	0.01548	0.0709	0.534
0.02080	0.01590	0.0683	0.531
0.02080	0.01498	0.0735	0.534

Table XXXVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02012	0.01410	0.0755	0.566
0.02012	0.01424	0.0758	0.572
0.02012	0.01382	0.0775	0.549

Table XXXVII.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25°.

m_1 .	m_2 .	v .	a .
0.02031	0.01498	0.0653	0.581
0.02031	0.01410	0.0800	0.577
0.02031	0.01402	0.0759	0.559

Table XXXVIII.—*Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, as Determined by Different Observers.*

<i>t.</i>	<i>m.</i>	<i>a.</i>	
		0.533	(Campetti ¹)
25°	0.0093	0.523	(Carrara)
25°	0.10	0.5797	(Jones and Bassett)
25°	0.02	0.572	(Jones and Rouiller)

The results obtained both by Jones and Bassett and by ourselves are considerably higher than the values given by the two Italian chemists.

Table XXXIX.—*Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents.*

<i>t.</i>	Percentage of Methyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.542	0.559	0.525	0.561
25°	0.540	0.529	0.533	0.562	0.572

The determinations of Jones and Bassett, working with 0.1 N solutions in mixtures of water and ethyl alcohol are given in the following table :

Table XL.—*Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents, as Determined by Jones and Bassett.*

<i>t.</i>	Percentage of Methyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.5628	0.5379	0.5299	0.5673	0.5871
25°	0.5285	0.5538	0.6010	0.5902	0.5797

The values in Table XXXIX. are plotted as curves in Fig. IX. A study of this figure shows that at 0°, the addition of 25 per cent of alcohol to the solution produces a fall in the relative velocity of the anion, but as the proportion of alcohol is increased the value for the transport number of the $\overline{\text{NO}_3}$ ion

¹ Campetti's original paper was not available, and the abstract in the Z. physik. Chem. gives neither temperature nor concentration.

again increases. A still further addition of alcohol again produces a depression in the curve, while in pure alcohol the relative velocity of the anion reaches a maximum value. A similar succession of rises and falls in the curve for the transport number was observed by Goldberger¹ for barium chloride, in mixtures of water and ethyl alcohol. With 0.1 N solutions of silver nitrate, Jones and Bassett obtained a pronounced minimum in the 50 per cent methyl alcohol mixture. At 25° the curve shows that the addition of alcohol produces a slight low-

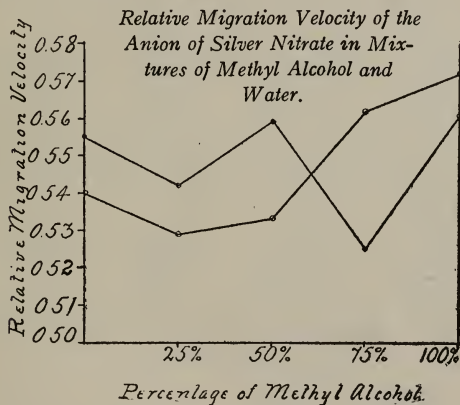


Fig. IX.

ering of the transport number, until the proportion of alcohol is raised to about 50 per cent. Further addition of alcohol produces a rapid increase in the relative velocity of the anion. Jones and Bassett, on the other hand, find that for the 0.1 N solution there is a sharp maximum in the 50 per cent mixture. A comparison of Tables XXXIX. and XL. shows that in solutions of different concentration the effect of the solvent on the migration velocities of the two ions is widely different.

¹ Roth : Z. physik. Chem., 42, 209 (1903).

Table XLI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02042	0.01605	0.0569	0.543
0.02042	0.01654	0.0527	0.537
0.02046	0.01427	0.0843	0.534
0.02046	0.01342	0.0925	0.543
0.02042	0.01582	0.0582	0.564

Table XLII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02073	0.01777	0.0369	0.549
0.02073	0.01810	0.0358	0.537
0.02073	0.01799	0.0361	0.541

Table XLIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02052	0.01573	0.0588	0.576
0.02052	0.01593	0.0588	0.570
0.02052	0.01540	0.0616	0.593

Table XLIV.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 0° .

m_1 .	m_2 .	v .	a .
0.02000	0.01569	0.0487	0.625
0.02000	0.01587	0.0494	0.610
0.02000	0.01542	0.0519	0.627

Table XLV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 25° .

m_1 .	m_2 .	v .	a .
0.02064	0.01450	0.0820	0.528
0.02064	0.01467	0.0821	0.535
0.02064	0.01409	0.0821	0.545
0.01980	0.01556	0.0536	0.532
0.01980	0.01609	0.0530	0.517
0.01980	0.01589	0.0538	0.516

Table XLVI.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02089	0.01590	0.0662	0.536
0.02089	0.01633	0.0649	0.521
0.02089	0.01581	0.0654	0.524

Table XLVII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02063	0.01603	0.0583	0.560
0.02063	0.01622	0.0579	0.563
0.02063	0.01600	0.0576	0.553

Table XLVIII.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25°.

m_1 .	m_2 .	v .	a .
0.02001	0.01717	0.0328	0.616
0.02001	0.01691	0.0364	0.633
0.02001	0.01672	0.0372	0.598

Table XLIX.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at Various Temperatures, as Determined by Different Observers.

t .	m .	a .	
3°.8–5°	0.150	0.573	(Hittorf)
20°	0.108	0.594	(Mather)
25°	0.076–0.101	0.5988	(Jones and Bassett)
25°	0.020	0.616	(Rouiller)

In ethyl alcohol also, as this table shows, the velocity of the anion increases with the dilution.

Table L.—Relative Velocity of the Anion of Silver Nitrate in Water, Ethyl Alcohol and Mixtures of These Solvents.

	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.544	0.542	0.580	0.621
25°	0.540	0.529	0.527	0.559	0.616

As Table L. and Fig. X. show, at both 0° and 25° the relative velocity of the anion, in mixtures of ethyl alcohol with water, decreases slightly as the proportion of alcohol is increased, but reaches a minimum in the 50 per cent mixture.

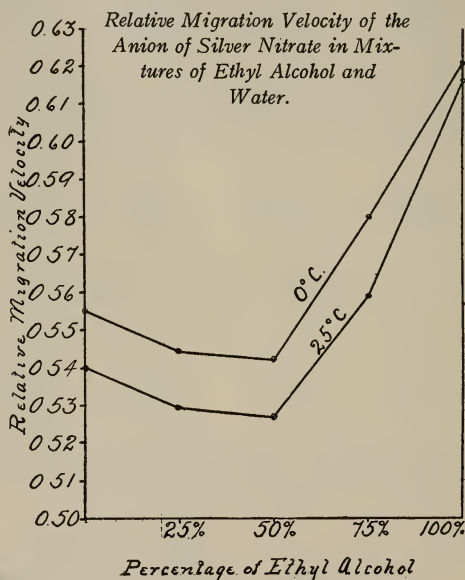


Fig. X.

From this point, increasing quantities of alcohol produce a very rapid rise in the relative velocity of the NO_3^- ion. With increasing temperature the two ions, in all these mixtures, tend to move with velocities that are more nearly equal.

Table LI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02061	0.01565	0.0677	0.537
0.02061	0.01534	0.0706	0.533

Table LII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02090	0.01601	0.0647	0.552
0.02090	0.01549	0.0688	0.561

Table LIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02082	0.01598	0.0617	0.575
0.02082	0.01558	0.0647	0.579

It was found that the most concentrated solution of silver nitrate in acetone, that could be prepared by long-continued shaking of the salt with the liquid at room temperature, contained less than 0.01 gram-molecular weight of the salt to the liter. With such dilute solutions it was impracticable to make a determination of the transport number.

Table LIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02061	0.01301	0.1023	0.528
0.02061	0.01275	0.1098	0.530
0.02061	0.01169	0.1139	0.528

Table LV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02110	0.01270	0.1106	0.540
0.02110	0.01301	0.1109	0.540
0.02110	0.01248	0.1092	0.543

Table LVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02100	0.01517	0.0713	0.581
0.02100	0.01567	0.0706	0.559
0.02100	0.01518	0.0702	0.571

Table LVII.—Relative Velocity of the Anion of Silver Nitrate in Water, Acetone and Mixtures of These Solvents.

<i>t.</i>	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.535	0.556	0.577	. .
25°	0.540	0.529	0.541	0.570	. .

The values in Table LVII. are plotted as curves in Fig. XI. There is a pronounced minimum in the 25 per cent acetone

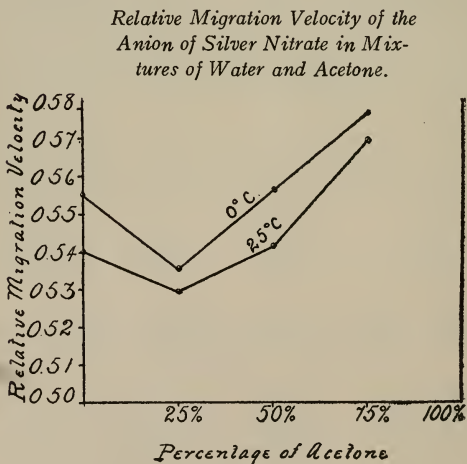


Fig. XI.

mixture. As in the mixtures with ethyl alcohol and water, the difference between the velocities of the anion and cation decreases with rise in temperature.

Table LVIII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02004	0.01105	0.1139	0.576
0.02004	0.01023	0.1192	0.587

Table LIX.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.01996	0.01407	0.0718	0.599
0.01996	0.01376	0.0755	0.583

Table LX.—Relative Velocity of the Anion of Silver Nitrate in Methyl and Ethyl Alcohols and Mixtures of These Solvents.

t .	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.581	0.591	. .	0.621

The relative velocity of the anion in mixtures of methyl and ethyl alcohol, increases uniformly with the proportion of ethyl alcohol. This is entirely analogous to the results obtained in measuring the conductivities of solutions in mixtures of the two alcohols.

Table LXI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02036	0.01084	0.1304	0.533
0.02036	0.01006	0.1378	0.536

Table LXII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02038	0.01312	0.0934	0.569
0.02038	0.01276	0.0966	0.563

Table LXIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02037	0.01539	0.0580	0.627
0.02037	0.01498	0.0620	0.620

Table LXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02020	0.01541	0.0583	0.584
0.02020	0.01545	0.0599	0.588
0.02020	0.01505	0.0617	0.563

Table LXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02028	0.01549	0.0556	0.613
0.02028	0.01570	0.0534	0.634
0.02028	0.01578	0.0498	0.609

Table LXVI.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents.

t .	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.534	0.566	0.623	. .
25°	0.572	0.578	0.619	. .	. .

Table LXVI. (Fig. XII.) shows that in methyl alcohol and acetone the transport number of the anion has a minimum

*Relative Migration Velocity of the Anion
of Silver Nitrate in Mixtures of Methyl
Alcohol and Acetone.*

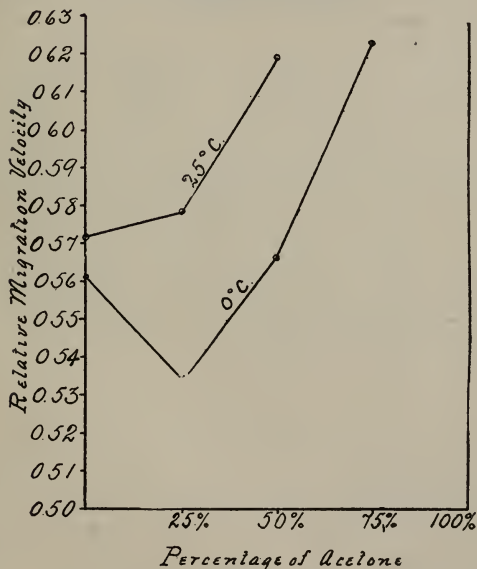


Fig. XII.

value, at 0°, in the mixture containing 25 per cent of acetone. At 25° the minimum has disappeared. It is interesting to note that in these mixtures the relative velocity of the anion increases with rise in temperature.

Table LXVII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02003	0.01421	0.0730	0.564
0.02003	0.01454	0.0690	0.580

Table LXVIII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02001	0.01451	0.0643	0.585
0.02001	0.01493	0.0634	0.586
0.02001	0.01461	0.0665	0.579

Table LXIX.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents.

t .	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.621	0.572	0.583		

In ethyl alcohol and acetone, there is a pronounced minimum in the relative velocity of the anion in the mixture containing 25 per cent of acetone.

PART III.

Discussion of Results.

Changes produced in the relative migration velocities, or transport numbers of the ions of an electrolyte, by varying the nature of the solvent, may be due to three causes:

1. Owing to some property peculiar to one of the ions, its velocity may be influenced by the solvent more than the velocity of the ion with the opposite charge.

2. Complex ions may be formed, which are more or less dissociated, according to the nature of the solvent, into simpler ions.

3. The ions may combine with the solvent itself.

That ions do combine with the solvent in many cases has been established, especially by the work of Jones and his pupils in this laboratory. But, if this is to affect the *relative*

velocities of the positive and negative ions, the solvent must combine with only one ion, or *different* quantities of it must combine with anion and cation, respectively. This, in substance, is the view proposed by Jones and also by Kohlrausch.¹ "About every ion there moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ions. . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent, diminishes as the atmosphere becomes of greater thickness. . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of the water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving, univalent ion, Li."

It has been attempted to show experimentally that the solvent does, in some cases, unite with only one, or in greater quantities with one ion. Thus, Oppermann,² by electrolyzing silver acetate in a mixture of acetic acid and water, concluded that the ion CH_3COO carries with it 6 more molecules of water than the silver. Working along the same lines with silver nitrate in methyl alcohol and water, Lobry de Bruyn³ obtained negative results. Morgan and Kanolt,⁴ using essentially the apparatus devised by Jones and Bassett, thought they found that in mixtures of water and ethyl alcohol the cation of silver nitrate carries along with it 1 molecule of water more than the anion. Their experimental work is, however, far from convincing, and their erroneous statement that the results of Jones do not show whether it is the free ions that are combined with solvent molecules, could easily have been

¹ P. Roy. Soc., 71, 338 (1903).

² Dissertation, Göttingen, 1901.

³ Rec. Trav. Chim., 22, 430 (1903).

⁴ J. Am. Chem. Soc., 27, 572 (1906).

avoided by simply reading the recent papers of Jones and Bassett.¹ In pyridine and water the silver ion carries, according to them, pyridine to the cathode.

The fact that the transport numbers of the ions of many simple binary electrolytes, where the possibility of the formation of complex ions is very doubtful, change with the dilution until they reach a constant value, is in harmony with the Kohlrausch view. That there is preferential combination of the solvent with one of the ions we cannot prove directly for pure solvents, but, if we arrange electrolytes in groups, according to the power of forming hydrates in solution, as determined by Jones and his co-workers, we find that, in general, *the power of forming hydrates is, in some way, dependent on the nature of the cation and more or less independent of the anion.* Thus, sodium, potassium and ammonium salts fall in the group showing the least tendency to form hydrates. Iron and aluminium salts form complex hydrates, while calcium, strontium and magnesium salts are intermediate between them and the alkali salts. If we compare these facts with the phenomena exhibited by transport numbers, we find that the relative velocities of the cations of salts with small power of hydration are practically independent of the concentration, while the transport numbers of such ions as calcium, strontium and magnesium, increase with the dilution. It is true that this may be due largely to the presence of complex ions in the more concentrated solutions, but the relative velocity of the cation of lithium chloride which, alone of the alkali chlorides crystallizes with water of crystallization, also increases considerably with the dilution. This can hardly be due to the presence of complex ions in the more concentrated solutions.

The data for transport numbers in non-aqueous solvents, at different dilutions, are too meagre to show whether this is true for other solvents than water. That it holds for silver nitrate in pyridine and acetonitrile has been shown by Schlundt.

Silver nitrate in water is a striking exception. The velocity of the anion increases with the dilution. It should be noted, however, that the nitrates of sodium and potassium exhibit

¹ THIS JOURNAL, 33, 583 (1905); 34, 346 (1906).

the same phenomena, although not quite so strikingly. The relative velocities of the cations of these salts decrease slightly with the dilution. It would seem, therefore, that in these salts it is the anion that is combined with the larger amount of the solvent.

Increase in temperature, as shown by Jones, would have a tendency to break up hydrates in solution. It has been found experimentally that, in most cases, raising the temperature increases the relative velocity of the slower ion.

That the relative ionic velocities for certain electrolytes are affected by the presence of complex ions, at least in the more concentrated solutions, is generally accepted. Reference need only be made to the classical case of cadmium iodide, which was first studied by Hittorf, and has since been the subject of a large number of investigations. As there is little probability that silver nitrate forms complex ions, this point will not be discussed in the present paper.

Finally, that the fluidity of the solvent affects the migration velocities is true beyond doubt, but how it affects the *relative* velocities we cannot as yet say. It is, of course, impossible to obtain solutions containing ions of only one kind and measure their viscosities, so that we are unable to determine, for any electrolyte in a given solvent, whether the friction of ion against solvent is greater for the cation than for the anion, or *vice versa*. In the present state of our knowledge, the influence of size and configuration on relative ionic velocities is also unknown. It may be stated that, in the course of this investigation, although working with solvents having such widely different fluidities as water, methyl and ethyl alcohols and acetone, it has not been possible to trace any connection between the transport numbers of the same ion and the fluidities of the solvents. This can be seen from the table given below. The values for the fluidities of the solvents are taken from the work of Jones and Bingham (see Table LXX.).

That there is any connection between the influence of the solvent on transport numbers and the nature of the charge carried by the ion, is very improbable. If there were any such connection, the influence of one solvent on different ions

with the same kind of charge, other things being equal, would always be in the same direction ; in other words, it would always increase the relative velocity of the anion, or *vice versa*. Here again, the lack of data for transport numbers of suffi-

Table LXX.—Relative Migration Velocity of the Anion of Silver Nitrate in Water, Methyl and Ethyl Alcohols and Acetone, with the Fluidity of These Solvents, at 0° and 25°.

Solvent.	0°.		25°.	
	Fluidity.	Transport No.	Fluidity.	Transport No.
Water	56.24	0.555	112.3	0.540
Methyl alcohol	122.20	0.561	176.7	0.572
Ethyl alcohol	53.88	0.621	90.35	0.616
Acetone	244.10	>0.620	308.9	>0.620

ciently dilute solutions in non-aqueous solvents, makes it impossible to draw any general conclusion as to the existence or non-existence of such a relation.

Since, from the increase with the dilution, of the relative velocity of the anion of silver nitrate in water, it would seem that the negative ion is combined with a greater quantity of the solvent, we should expect the addition to the solution of some "dehydrating agent," such as alcohol, would have the same effect as an increase in concentration in the water solution ; in other words, *a decrease in the relative velocity of the anion*. That this is true for ethyl alcohol up to the 50 per cent mixture, and that the increase is slightly more marked at 0° than at the higher temperature, as would be expected, is shown by Fig. X. As the relative velocity of the anion in pure alcohol is much larger than in water, increasing amounts of alcohol will tend to retard the cation, and beyond the 50 per cent mixture the effects of decreasing hydration are entirely masked and the relative velocity of the anion increases rapidly.

In this connection, attention should be called to the work of Lobry de Bruyn and Jungius¹ and of Bruni and Manuelli,² who have shown, by cryoscopic methods, that certain hydrated salts, when dissolved in organic solvents, retain part of their water of crystallization.

¹ Rec. Trav. Chim., 22, 421 (1903).

² Z. Elek. Chem., 10, 601 (1904).

Looking at Fig. IX., it will be seen that what has been said for ethyl alcohol and water is true of methyl alcohol and water at 25°. But the increase in the relative velocity of the cation with the addition of alcohol to the solvent is not so marked, and the influence in the opposite direction of increasing amounts of alcohol, already manifests itself in the 50 per cent mixture. The curve for the transport number of the anion at 0° shows a minimum in the 25 per cent mixture, but beyond the 50 per cent mixture it is abnormal. No explanation for this can as yet be offered.

Although we have no experimental evidence that proves directly that in water and acetone the anion of silver nitrate is more "hydrated" than the cation, yet, by analogy with the alcohol and water mixtures, we should expect this to be the case. A study of Fig. XI. will show that in these mixtures there is at first a decrease, which is more marked at the lower temperature, in the relative velocity of the anion as alcohol is added to the solution. The turning point in the direction of the curve, however, is already reached in the mixture containing only 25 per cent of acetone. This is what we should expect if the effect of pure acetone on the relative ionic velocities of the anion and cation is taken into account. Although we have been unable to determine the transport numbers in pure acetone, all measurements made with mixtures containing increasing quantities of it tend to show that in the pure solvent the relative velocity of the anion is greater even than in pure ethyl alcohol. It is not surprising, therefore, that the addition of more than 25 per cent to an aqueous solution should entirely offset the effect of decreasing hydration and produce an increase in the relative velocity of the anion.

The results for mixtures of methyl alcohol and acetone are of the same nature. As with mixtures of water and acetone, we have no direct evidence that one ion carries more of one of the constituents of the solvent mixture than the ion of opposite charge. But a study of Fig. XII. makes it seem probable that the anion carries methyl alcohol with itself. At 0°, as the proportion of acetone is increased, the value for the transport number of the anion passes through a pronounced mini-

mum in the 25 per cent mixture. At 25° there is no actual minimum, but up to the 25 per cent mixture there is practically no increase in the relative velocity of the anion. It is interesting to note that in these mixtures, although the transport number of the anion is less at 0° than at 25°, the influence of the solvent is, as usual, more pronounced at the lower temperature.

The data for mixtures of ethyl alcohol and acetone (Table LXIX.) are too fragmentary to make any generalization possible, yet they show that the relative velocity of the anion passes through a minimum in the mixture containing 25 per cent of acetone.

The striking parallelism exhibited by calcium and silver nitrates, when their conductivity phenomena in binary mixtures of acetone with water and methyl and ethyl alcohols are compared, is very interesting in view of certain relations observed by Jones and Bingham between the conductivities of potassium iodide, calcium nitrate and lithium nitrate, and the migration velocities of the cations of these salts. Our conductivity measurements confirm the conclusions reached by them, but as it has no direct bearing on this investigation, reference only is made to their work.¹

Summary.

1. We have measured the conductivity of silver nitrate in acetone, and in binary mixtures of this solvent with water, methyl alcohol and ethyl alcohol. The results were of the same general nature as those obtained by Jones and Bingham for calcium nitrate.

2. The transport number of the anion of silver nitrate in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone has been determined at two temperatures, 0° and 25°.

3. That increase in temperature, in general, increases the velocity of the slower ion has been confirmed. Solutions in mixtures of methyl alcohol with acetone, in pure methyl alcohol and in a 75 per cent mixture of methyl alcohol with water are exceptions.

¹ THIS JOURNAL, 34, 481 (1905).

4. It has been shown that the nature of the solvent very materially affects relative migration velocities. That this is due to varying degrees of combination of the solvent with one of the ions, as compared with the ion of opposite charge, is very probable.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contribution from the Kent Chemical Laboratory of the University of Chicago.
ON THE CONSTITUTION OF THE ACETYLIDENE
COMPOUNDS.

BY JAMES WRIGHT LAWRIE.

It is now 9 years since Nef came to the conclusion that certain halogen substitution products of the hydrocarbon, C_2H_2 , were acetylidene compounds,¹ containing bivalent carbon. At that time it seemed probable that 2 series of halogen substitution products of C_2H_2 might exist; namely, the monohalogen acetylenes, $XC : CH$, and the corresponding halogen substituted acetylidenes, $H CX : C$, as well as the halogen disubstituted acetylenes, $XC : CX$, and the isomeric dihalogenated acetylidenes, $X_2C : C$. This has since been found not to be the case and it is now certain that the so-called mono- and dihalogenated acetylenes are *all* acetylidene compounds; furthermore, tautomeric conceptions cannot be applied here to explain the non-existence of their isomers—the real mono- and dihalogen substituted acetylenes.

The sweet smelling, harmless, monoiodacetylene of Paterno and Peratoner² does not exist, but has been shown by Peratoner and Spallino³ to consist of a mixture of acetylene, vinyl chloride, ethylidene chloride and acetylene diiodide. The isomeric, poisonous substance described by Baeyer as iodacetylene⁴ has been proved by Nef⁵ to be diiodacetylidene. On the other hand, halogen substitution products of monoalkylated and monoarylated acetylenes as $CH_3C : Cl$ and $C_6H_5C : CX$

¹ Ann. Chem. (Liebig), 298, 332 (1897).

² Gazz. chim. ital., 19, 584.

³ Ber. d. chem. Ges., 34, 2718–20 (1901).

⁴ *Ibid.*, 18, 2274.

⁵ Ann. Chem. (Liebig), 308, 325–6 (1899).

(X = Cl, Br, or I) have since been isolated by Nef;¹ their properties—sweet smelling, harmless—are in marked contrast to those of the acetylidene compounds which are all very poisonous and spontaneously combustible substances.

Nef's proof of the constitution of the acetylidene compounds is as follows:² The perhalogen ethylenes, $X_2C : CX_2$, lose, on treatment with alcoholic potassium hydroxide, one pair of halogen atoms, giving, in the case where X represents iodine, C_2I_2 , and where X is bromine the corresponding alcoholate of C_2Br_2 , namely, ethyl dibromvinyl ether, $C_2Br_2HOC_2H_5$, whose constitution, as was sharply proved by him, must be represented by the formula $Br_2C : CHOC_2H_5$. Nef, therefore, assumed that in the latter case dibromacetylidene must first be formed, but being too reactive, it at once absorbed the alcohol present, giving the unsymmetrical ethyl dibromvinylether; he, in fact, made many attempts to isolate the intermediate product, dibromacetylidene, but without success. Quite recently Lemoult has isolated this compound by the action of alcoholic potassium hydroxide on tribromethylene, $Br_2C : CHBr$, in the cold; he, however, considers it to be dibromacetylene.³ Lemoult obtained from it an addition product with iodine, which, from its properties, melting point 95° , etc., is obviously identical with Nef's unsymmetrical dibromdiiodethylene, $I_2C : CBr_2$.⁴ It was, therefore, evident that the constitution of all the halogen substituted acetylidenes could now be determined with absolute precision and, consequently, I began experiments in this direction at the suggestion and under the guidance of Dr. Nef. Our expectations have been realized; my results confirm in every detail the conclusions previously reached by Nef. Briefly stated, the evidence now establishing the constitution of the acetylidene compounds is the following: Dibromacetylidene gives, with hydrogen iodide at ordinary temperatures, the addition product dibromiodethylene, C_2Br_2HI , as a heavy oil, boiling at 91° (15 mm.). This product must possess the constitution represented by the formula $Br_2C : CHI$,

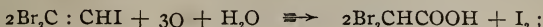
¹ Ann. Chem. (Liebig), **308**, 292-323.

² *Ibid.*, **298**, 336, 340-1.

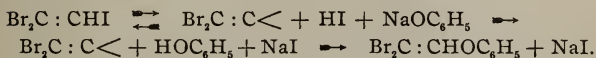
³ Bull. Soc. Chim. de Paris, **43**, 193. Cf. Compt. rend.; **136**, 1333; **137**, 55; **139**, 131.

⁴ Ann. Chem. (Liebig), **298**, 353.

first, because it can be converted smoothly, by oxidation with fuming nitric acid at -10° , into iodine and dibromacetic acid,



second, because it gives, on treatment with alcoholic sodium phenolate, a large yield of unsymmetrical phenyl dibromvinyl ether, according to the equation



That the two bromine atoms in phenyl dibromvinyl ether are bound to one and the same carbon atom is certain, because this compound can be converted, almost quantitatively, by fuming nitric acid, at -10° , into isomeric nitrated phenyl dibromacetates, $\text{Br}_2\text{CHCOOC}_6\text{H}_3(\text{NO}_2)_2$, which give, on treatment with dilute or concentrated cold, aqueous ammonia, the isomeric dinitrophenols and dibromacetamide. From this, it follows definitely that dibromacetylidene has its two bromine atoms bound to one and the same carbon atom. Since dibromacetylidene diiodide, $\text{Br}_2\text{C} : \text{CI}_2$, and diiodacetylidene dibromide are proved to be identical as regards their chemical and physical properties, it follows, further, that diiodacetylidene must possess the constitution represented by the formula $\text{I}_2\text{C} : \text{C}$. Finally, since Nef has shown that bromacetylidene gives, with iodine, the addition product,¹ $\text{BrCH} : \text{CI}_2$, which, on treatment with alcoholic potassium hydroxide or potassium acetate, gives potassium bromide and diiodacetylidene, the conclusion is unavoidable that in bromacetylidene the halogen and hydrogen atoms are both bound to the same carbon atom, as represented by $\text{BrCH} : \text{C}$. The so-called chloracetylene of Wallach² must, therefore, also be represented by the acetylidene formula, $\text{ClCH} : \text{C}$, since this compound possesses chemical and physical properties which, in every detail, resemble most strikingly those of the analogous bromacetylidene. The known mono- and dihalogen substitution products of acetylene, therefore, all belong to the acetylidene series ; the corresponding derivatives

¹ Ann. Chem. (Liebig), 298, 359.

² Ibid., 200, 88

of acetylene are unknown and it is exceedingly improbable that any such compounds can be isolated.

EXPERIMENTAL PART.

Properties of Dibromacetylidene.

All the dibromacetylidene used in my experiments was prepared according to Lemoult's later directions from tribromethylene in cold alcoholic solution in the presence of 1.5 molecules of potassium hydroxide. Dibromacetylidene boils at 76° and has sp. gr. about 2. Lemoult states in his first paper in the *Comptes rendus* that he obtained at least an 80 per cent yield, but he never succeeded in obtaining over 15 per cent of the pure product in his later work.¹ He was, finally, compelled to stop work on the subject because of many violent explosions. I also had one very serious explosion with dibromacetylidene and found, moreover, that it possesses an intensely nauseating odor, resembling that of diiodacetylidene and of the isocyanides. The substance is intensely poisonous, causes headaches, indigestion and feelings of exhaustion, with most noticeable loss of memory. Terrific explosions may take place without the slightest warning when handling the substance in an atmosphere of carbon dioxide or of nitrogen; these are, undoubtedly, due to the presence of a trace of oxygen, which causes the dibromacetylidene to burn locally with violence; a sudden dissociation of the main product into bromine and diatomic carbon then results,



The explosions in this case, as well as in that of acetylene and its heavy metal salts and the other halogenated acetylidenes must, therefore, all be attributed to the tremendous energy of the diatomic carbon.² It should be emphasized in this connection that Nef, in all his experiments with bromacetylidene, never had an explosion, whereas Wallach found that chloracetylidene often exploded spontaneously, in an inert atmosphere. It is, therefore, certain that all these substances can

¹ Bull. Soc. Chim. de Paris, 43, 193.

² Nef: Ann. Chem. (Liebig), 298, 348.

be handled without danger, but rigid precautions must be taken to ensure the absence of all traces of oxygen; it requires, furthermore, the constant presence of at least two persons to handle the substances properly. In view of all these experiences, I finally carried out most of my experiments with crude dibromacetylidene, and took special precautions never to inhale its vapors; the pure substance was handled only when absolutely necessary.

Crude dibromacetylidene, containing unchanged tribromethylene and traces of ethyl bromacetate and unsymmetrical ethyl dibromvinyl ether, can be prepared with the greatest ease, in the following manner: Twenty-six and one-half grams of tribromethylene and 1.5 molecules of potassium hydroxide (10.5 grams of 82 per cent KOH) are mixed in cold, alcoholic solution in a nitrogen atmosphere, care being taken to use the least possible amount of 95 per cent spirit, 35–50 grams, and the mixture is kept cool by running water, or by shaking in a large pail of ice-water. The operation is best carried out in a separatory funnel of about one liter capacity, provided above with a two-holed rubber stopper in which are inserted a small dropping funnel and a bent glass stop-cock. After 2 hours 400–500 cc. of cold water, freed from air, is slowly added and the larger part of the dibromacetylidene, besides other products, separates out at the bottom as a heavy oil, 12.1 grams, which can then be drawn off below and collected in a proper receiver, filled with dry carbon dioxide or nitrogen; this oil can at once be distilled from the receiver, the only product which passes over when the temperature of the surrounding oil-bath is 100°–120° being dibromacetylidene. For most purposes, however, the crude oil, 12.1 grams, containing about 7 grams of dibromacetylidene was used directly. In this operation about one-third of the dibromacetylidene formed in the reaction is lost because it remains dissolved in the supernatant, aqueous-alcoholic solution. It was found that 2 hours' standing of the reaction mixture gave the best results, since by longer standing the dibromacetylidene is slowly converted into monobromacetylidene. It was easily possible to establish this point, as well as the nature of the other products formed in the reaction,

in the following manner : The crude oil separated off by addition of much water, or the original reaction mixture, after standing from 2 to 24 hours, was treated, in alcoholic solution, with an excess of finely powdered iodine (25 grams) and allowed to stand for 2 days at the ordinary temperature. In this way all the mono- and dibromacetylidene present are converted into their corresponding iodides, $\text{BrCH} : \text{Cl}_2$ and $\text{Br}_2\text{C} : \text{Cl}_2$; the former is a liquid, boiling at 115° (15 mm.) and the latter a crystalline solid which is left behind in the distilling flask after all the other products present have been distilled over under reduced pressure. The method of procedure, therefore, was to add much water to the iodine mixture and extract well with ether; the ethereal solution was then washed with aqueous sodium hydroxide, to get rid of the iodine and the oils left, after drying with calcium chloride and removing the ether, were distilled under reduced pressure. Ethyl bromacetate, tribromethylene and unsymmetrical dibromvinyl ethyl ether boil at 159° , 163° and 170° under ordinary pressure; they are, therefore, found in the lower boiling fractions and are then separated and identified according to Nef's directions;¹ the higher boiling fraction, 100° – 115° (15 mm.), is found to consist chiefly of bromacetylidene diiodide, which is readily identified by treatment with alcoholic potassium hydroxide and subsequent conversion of the crude diiodacetylidene formed² into periodethylene (m. p. 184°). The presence of these substances in the reaction products of alcoholic potassium hydroxide on tribromethylene is self-evident from the work of Nef. It was noticed, in this way, that the yield of dibromacetylidene diminishes, while that of bromacetylidene increases if the original alcoholic potassium hydroxide solutions of tribromethylene are allowed to stand longer than 2 hours in the cold. This proves that dibromacetylidene is slowly transformed, on standing in cold, slightly alkaline solution, or more rapidly on heating into bromacetylidene, and this explains why Nef failed to isolate dibromacetylidene in his experiments with tribromethylene and alcoholic potassium hydroxide.

¹ Ann. Chem. (Liebig), 298, 334–36.

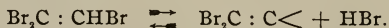
² *Ibid.*, 298, 359.

In an experiment where 26.5 grams of tribromethylene, 50 parts of alcohol and 10.5 grams of 82 per cent potassium hydroxide were used, the reaction mixture, after 2 hours' standing in the cold, gave, on treatment with 25 grams of iodine, 24.6 grams of pure dibromdiiodethylene, melting at 95° ; this proves that 56.2 per cent of the theoretical amount of dibromacetylidene is formed under these conditions. When I used the same amounts of the reagents, but allowed the mixture to stand 24 hours, at room temperature, before adding iodine, only 18.1 grams of dibromdiiodethylene, 41.1 per cent of the theory and 7.1 grams of crude diiodbromethylene, b. p. 100° – 115° (15 mm.) were obtained, whereas the amount of the latter substance isolated in the first experiment was only 3 grams. The 7.1 grams of crude bromacetylidene diiodide obtained in the second experiment gave, on treatment with 1.3 grams of potassium hydroxide in 10 cc. of alcohol, and subsequent standing for 12 hours in the cold, potassium bromide and an oil, which, with 7 grams of iodine, in ethereal solution, gave, finally, 2.8 grams of pure periodethylene, melting at 184° . In addition, the presence of much unchanged tribromethylene and traces of unsymmetrical dibromvinyl ethyl ether, $\text{Br}_2\text{C}:\text{CHOC}_2\text{H}_5$, was established in the lower boiling fraction, 50° – 100° (20 mm.). In order to determine how much dibromacetylidene is present in the crude oil separated by the addition of much water, the following experiment was carried out: A mixture of 26.5 grams of tribromethylene, 35 grams of 95 per cent alcohol and 10.5 grams (82 per cent) potassium hydroxide were allowed to stand 2 hours, in the cold, and then 400 cc. of water were added. The oil which separated was allowed to run directly into 200 cc. of ether and 25 grams of iodine, etc. Only 16.9 grams of dibromdiiodethylene, 38.6 per cent of theory, were obtained, which proves that about one-third of the dibromacetylidene formed in the reaction must have remained in the aqueous-alcoholic solution. No bromacetylidene diiodide was obtained in this experiment; it is evident that only traces of bromacetylidene can be present in the oil separated by the addition of water, as the small amount of bromacetylidene formed in the reaction must practically all re-

main in the aqueous-alcoholic solution. The crude oil, 12.1 grams, which separates off by addition of water, therefore contains about 7 grams of dibromacetylidene; the other product present, as was often established by special experiments, is, chiefly tribromethylene containing traces of ethyl bromacetate and unsymmetrical dibromvinyl ethyl ether.

Dibromiodethylene,
 $\text{Br}_2\text{C} : \text{CHI}.$

All attempts to add alcohol, phenol, acetic, formic and trichloroacetic acid to dibromacetylidene, either at ordinary temperatures, or in sealed tubes at 100° , were attended with negative results; the addition of alcohol or phenol to this substance only takes place when it is set free in a *nascent condition* from tribromethylene by potassium hydroxide, sodium ethylate, or sodium phenolate, according to the equation



The salt present first removes one of the products of dissociation, the hydrogen bromide, and the active or nascent dibromacetylidene, before it can transform itself into inactive dibromacetylidene, $\text{Br}_2\text{C} : \text{C}]$, may absorb, in part or entirely, according to the speed of the reaction, the dissociated alcohol, $\text{H}-\text{OC}_2\text{H}_5$, or phenol, $\text{H}-\text{OC}_6\text{H}_5$, present, giving, thus, the addition products, $\text{Br}_2\text{C} : \text{CHOC}_2\text{H}_5$ and $\text{Br}_2\text{C} : \text{CHOC}_6\text{H}_5$. Nef has repeatedly made similar observations in his more recent work on the alkyl halides, alcohols, etc.¹ The dibromacetylidene, as such, contains, at 20° – 100° , too small a proportion of active particles,²



to be able to absorb readily such reagents as alcohol, water, ammonia, phenol, or acetic acid. It, however, absorbs with the greatest of ease such reagents as bromine, iodine, hydrobromic acid and hydrogen iodide. The addition product with hydrogen iodide is of especial interest, as it is possible, by

¹ Ann. Chem. (Liebig), **309**, 126–189; **310**, 316–335; **318**, 137–230; **335**, 191–333.

² Nef: J. Am. Chem. Soc., **26**, 1555, 1563.

means of it, to prove that the 2 bromine atoms in dibrom-acetylidene are bound to the same carbon atom.

Crude dibromacetylidene, from 26.5 grams of tribrom-ethylene,¹ is added, cooling with ice-water, to 40 grams of aqueous hydriodic acid, sp. gr. 1.96, which was first freed from all possible traces of free iodine by means of 2 grams of red phosphorus. There was a noticeable rise in temperature and the mixture was finally allowed to stand in a carbon dioxide atmosphere for 2 hours at the ordinary temperature; water was then added and the oil extracted with ether, washed with sodium hydroxide and dried with calcium chloride. On fractionation, under reduced pressure, 10 grams of dibromiodethylene were obtained. It is a sweet smelling oil, boiling at 91° (15 mm.) and having sp. gr. 2.952 at 24° (Westphal). In addition, 3 grams of dibromdiiodethylene, melting at 95°, were isolated from the residue left in the distilling flask. If no precaution is taken to free the hydrogen iodide used from iodine, practically only dibromdiiodethylene is obtained as the reaction product. Analysis:

0.2782 gram substance gave 0.5528 gram 2AgBr, AgI by the Carius method, and subsequent electrolysis of the 2AgBr, AgI, in potassium cyanide solution, gave 0.2985 gram, or 53.9 per cent silver instead of the theoretical 53.2 per cent Ag.

0.7031 gram substance gave 0.1972 gram CO₂ and 0.0225 gram H₂O.

	Calculated for C ₂ Br ₂ HI.	Found.
C	7.68	7.61
H	0.32	0.35
Br ₂ I	92.0	93.3

I attribute the high percentage of halogen found to the presence of mechanically enclosed silver nitrate.

A mixture of 10 grams dibromiodethylene, in 17 grams of

¹ A special experiment with 12.1 grams pure tribromethylene, 40 grams hydriodic acid, sp. gr. 1.96, and 2 grams of phosphorus proved that, after standing 2 hours at 0°, under the same conditions, therefore, as in the experiment given above, this substance remains entirely unchanged; for 10 grams tribromethylene, boiling at 73° (33 mm.), were recovered on working up the mixture in the usual manner. Furthermore, iodine, in ethereal solution, does not act on tribromethylene after standing for three weeks at the ordinary temperature.

alcohol containing 3.5 grams of potassium hydroxide, was allowed to stand at 0° for 2 hours; 12 grams of powdered iodine were then added and, after 12 hours' standing and working up as in the previous cases, 6.4 grams of dibromdiiodethylene, m. p. 95° , were obtained. This proves that a fair amount of dibromacetylidene must have been formed in the reaction.

On the Conversion of Dibromiodethylene into Dibromacetic Acid.

As mentioned in the introduction, dibromiodethylene, 10 grams, is transformed smoothly by 2 parts of fuming nitric acid, at -10° , into dibromacetic acid. The oil, which is added drop by drop to the acid, dissolves and iodine at once separates out; there is a noticeable rise of temperature which must be properly controlled by shaking. The mixture was finally allowed to stand a short time surrounded by ice-water and was then poured on ice, extracted 5 times with ether and the ethereal solution was freed from acids by extracting with dilute sodium carbonate solution. The alkaline solutions then gave, on acidifying, extracting 5 times with ether, etc., 5.7 grams of dibromacetic acid, b. p. 107° – 110° (30 mm.), m. p. 47° – 48° . The substance was further identified by dissolving 3.5 grams in 12 cc. of absolute alcohol and heating for 3 hours at 100° – 102° , in the presence of concentrated sulphuric acid; 3.6 grams of crude ethyl dibromacetate were obtained which, on treatment with 30 cc. of 10 per cent ammonia, at -5° , gave 1.9 grams of pure dibromacetamide, m. p. 156° , which was analyzed for halogen.

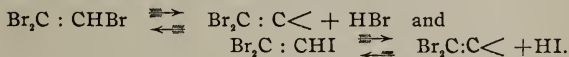
0.2105 gram substance gave 0.3629 gram AgBr (Carius).

	Calculated for $C_2H_3ONBr_2$ $\leftarrow ?$	Found.
Br	73.73	73.35

An entirely analogous experiment was carried out with 10 grams of tribromethylene and 20 grams of fuming nitric acid, but it was found necessary to heat the mixture to 100° in order to dissolve all the halogen compound. On working up the reaction products as above, 6 grams of dibromacetic acid, m. p. 40° , were obtained; 4.8 grams of this, heated with 10 grams of absolute alcohol and 2 grams of concentrated sul-

phuric acid, for 3 hours, at 105° , gave 4.5 grams of crude ethyl dibromacetate, from which, by means of 10 per cent ammonia, at -10° , 2.5 grams of pure dibromacetamide, m. p. 156° , were obtained. In this case a fair amount of neutral products was also isolated; these yielded 2.1 grams, at 108° – 110° (15 mm.) and, on cooling, 0.7 gram of perbromethylene, m. p. 53° – 54° , separated out. The oil remaining was tribromnitroethylene, $\text{Br}_2\text{C} : \text{CBrNO}_2$, obtained by Scholl and Brenneisen,¹ by the action of nitric acid on tribromethylene.

It is obvious that the conversion of tribromomethylene and of dibromodethylene into dibromacetic acid by nitric acid is due to a combustion of the dibromacetylidene, which is a common dissociation product in both cases:



The dibromacetylidene oxidizes first to dibromacetylidene oxide, $\text{Br}_2\text{C}:\text{CO}$, which then absorbs water or nitric acid, giving, finally, dibromacetic acid. This is shown also by the fact that tribromomethylene, as well as tetrabromomethylene, take up oxygen directly at low temperatures (50°), giving dibromacetyl bromide, Br_2CHCOBr , and tribromacetyl bromide, Br_3CCOBr , respectively. It is clear that the common dissociation product, $\text{Br}_2\text{C}:\text{C}$, first takes up one atom of oxygen and the oxide formed then unites at once with the other dissociation product present, HBr or Br_2 , to give the substances actually obtained.² It is clear that the experiments of Henry on trichlorovinyl ethyl ether,³ as well as those of Swarts on perhalogenated ethylenes and on dibromfluorethylene,⁴ must be interpreted in a similar manner.⁵ In repeating an

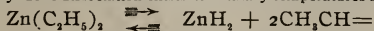
¹ Ber. d. chem. Ges., **31**, 651. Cf. Biltz and Kedesdy: *Ibid.*, **33**, 2191.

² Cf. Nef: *Ann. Chem. (Liebig)*, **298**, 365. Demole: *Ber. d. chem. Ges.*, **11**, 315; **12**, 2245. *Bull. Soc. Chim.*, **34**, 201. *Vide* also recent experiments of Bacon and Goldthwaite from this laboratory. *THIS JOURNAL*, **30**, 455; **33**, 75.

³ Ber. d. chem. Ges., 12, 1838.

⁴ Bul. Acad. Belg. [3], 35, 849; 36, 532. Centrabl., 1898, II., 702; 1899, I., 588.

⁶ Dr. Nef informs me that he now believes that the spontaneous combustibility of zinc ethyl (Cf. Ann. Chem. (Liebig), 298, 331, foot-note) undoubtedly depends upon the fact that ethylidene dissociation exists at ordinary temperatures according to

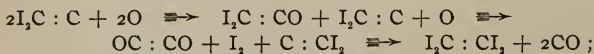


(Cf. Ann. Chem. (Liebig), 309, 165; 310, 317-335; 318, 1-55). The remarkable behavior of zinc ethyl towards chloroform, bromoform and carbon tetrachloride (Cf. Beilstein; working with Rieth and Alexeyeff, Ann. Chem. (Liebig), 124, 245 and Jahres. d. Chem., 1864, 470) may also be very simply explained on this basis.

experiment of Demole with 10 grams of tribromomethylene and dry oxygen, in a bath kept at 140° , I have found that besides 4.1 grams dibromacetyl bromide, b. p. 57° – 80° (11 mm.), 5.2 grams of oil boiling at 119° (11 mm.) are obtained; the latter solidified, in great part, on cooling, and was proved to be perbromethylene. The oil left, in all 7 grams, gave, on treatment with 30 cc. of 10 per cent ammonia, 2.4 grams of pure dibromacetamide, m. p. 156° . It is, therefore, evident that the conversion into dibromacetyl bromide is not quantitative. From the results obtained in the burning of dibromacetylidene itself (see below) it is exceedingly probable that some of the dibromacetylidene oxide first formed unites further with oxygen, giving bromine and carbon monoxide; the bromine must then naturally give with the tribromomethylene, or its product of dissociation, $\text{Br}_2\text{C}:\text{C}$, the perbromethylene which I obtained in such large quantity in my experiment. Finally, brief mention should be made of an attempt to oxidize dibromiodethylene, $\text{Br}_2\text{C}:\text{CHI}$, in the presence of dry oxygen, in a flask placed in a bath at 140° . It is obvious, from the theory of the reaction, that dibromacetylidene oxide and hydrogen iodide must first result, the hydriodic acid must then at once react with the oxygen present to give free iodine and detonating gas. This was proved in a most frightful manner by the explosion which took place when I, by inadvertence, applied the splinter test for oxygen to the gaseous mixture.

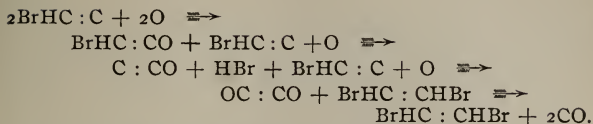
On the Oxidation of Dibromacetylidene in Dry Oxygen.

Nef¹ has shown that diiodacetylidene and bromacetylidene burn in the presence of oxygen to give chiefly carbon monoxide, periodethylene, or ethylene bromide, according to the following equations:

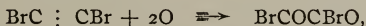


and

¹ Ann. Chem. (Liebig), 298, 345, 358.



It was, therefore, to be expected that dibromacetylidene would behave in a similar manner, giving 2 molecules of carbon monoxide and perbromomethylene. This was found to be the case; about 78.4 per cent of the oxidation takes place in this way, but some very interesting side reactions, which are theoretically self-evident, also occur. Lemoult¹ has studied the behavior of dibromacetylidene under water, or dissolved in alcohol, towards oxygen and finds that oxalic acid is a reaction product; he assumes that oxalyl bromide is first formed, according to the equation:



etc., but he gives no quantitative data and states that other products containing halogen are also formed. In my first experiments I tried the action of dry oxygen on dibromacetylidene dissolved in moist or in absolute ether, but found that, under these conditions, practically no oxidation takes place as the substance was recovered unchanged; the best condition for studying the behavior of this substance towards oxygen was, finally, found to be in the presence of absolute alcohol. Because of their interest, I shall first give, however, a brief summary of my experiments with dibromacetylidene and oxygen, in the presence of dry and moist ether.

Crude dibromacetylidene, made from 53 grams of tribromethylene, was separated by the addition of water, drawn off into a receiver filled with dry carbon dioxide and then heated² in an oil-bath up to 100°-120°. About 11 grams of pure dibromacetylidene, b. p. 76°, distilled over and was collected in a flask containing 70 cc. of ether and 5 cc. of water. The flask was now connected with a small gasometer filled with water,

¹ *Loc. cit.*

² In an experiment in which I attempted to repeat this operation, the dibromacetylidene exploded with terrific violence the moment the oil struck the bottom of the receiver. I imagine traces of air must have been left in the receiver.

with three intervening wash bottles containing 30 per cent potassium hydroxide to absorb any carbon dioxide formed in the reaction. Dry oxygen was then allowed to bubble slowly through the ethereal solution of dibromacetylidene, at the rate of 700 cc. per hour, for 6 hours; the gaseous products naturally collected in the small gasometer. No trace of carbon monoxide was formed, as determined by absorbing the gases first by pyrogallol and then by ammoniacal cuprous chloride. The ether solution was now distilled over on a water-bath into a receiver containing iodine; 16.3 grams of dibromacetylidene diiodide, m. p. 95° , were obtained on working up in the usual manner, which shows that the dibromacetylidene had not been acted upon. An experiment, using absolute ether and crude dibromacetylidene gave an entirely similar result. It was now observed that ethereal solutions of dibromacetylidene could be poured from flask to flask and exposed to the air without the slightest fuming; one can even distil off most of the ether by means of a Glinsky apparatus and the oil left, which still contains small amounts of ether, burns only very slowly at the ordinary temperature. It can be poured into a distilling flask and then be fractionated under reduced pressure; on opening the Brühl apparatus the dibromacetylidene fraction, 37° (60 mm.), burns with great violence at once in the air; there is no explosion, however, but the Brühl apparatus becomes entirely covered with soot. A special examination of the residue, about 12 grams, after the 11 grams of dibromacetylidene, mentioned above, from 53 grams of tribromomethylene had been removed by heating in an oil-bath at 100° – 120° , gave the following result: Two fractions, besides 5 grams of non-volatile tar, were obtained on distillation under reduced pressure; the lower fraction, 0.8 gram, b. p. 67° – 75° (17 mm.), possessed the sharp odor of ethyl bromacetate; the other boiled at 108° – 110° (12 mm.) and solidified at once on cooling, giving 4 grams of crystals of perbromomethylene¹, m. p. 55° – 56° . The lower boiling fraction gave, on treatment with ammonia, a trace of bromacetamide; the oil left had now lost its

¹ No perbromomethylene, C_2Br_4 , is present in crude dibromacetylidene; its presence here is probably due to a dissociation of C_2Br_2 into Br_2 and C_2 with subsequent absorption of Br_2 by C_2Br_2 to form C_2Br_4 .

pungent odor and gave, on treatment with concentrated nitric acid in the cold, a neutral, oily mixture which, on treatment with ammonia, gave a very small amount of crystals of dibromacetamide, m. p. 156° , thus proving the presence of asymmetrical dibromovinyl ether. Finally, there was left an insoluble, neutral, sweet smelling oil, possessing all the properties of tribromethylene (this was the main product).

On the Oxidation of Dibromacetylidene in the Presence of Alcohol.

Crude dibromacetylidene, from 53 grams of tribromethylene and containing, therefore, according to the quantitative conversion into iodide, given above, 14 grams of dibromacetylidene was run into a flask, filled with carbon dioxide, containing 50 grams of absolute alcohol; the flask was connected with the usual train of 3 washing bottles containing 30 per cent potassium hydroxide and, finally, with the gasometer filled with water. Dry oxygen was then passed through the mixture, which was cooled with ice-water and shaken continually at first, at the rate of 1 liter per hour for 3.5 hours, during which time the temperature of the surrounding water was allowed to go up to 20° . There was a slight fuming noticed at the beginning and at the end no trace of unchanged dibromacetylidene could be detected in the alcoholic solution. The analysis of the gaseous mixture which had collected in the gasometer gave, at 20° and 755 mm., 800 cc. of carbon monoxide from a total volume of 2550 cc. The excess of oxygen present in 100 cc. was first absorbed by pyrogallol, and the carbon monoxide left was then determined by ammoniacal cuprous chloride. The amount of carbon monoxide which can be formed, according to the equations given above, from 14 grams of dibromacetylidene is 1.7 liters. Hence, about 47 per cent of the theoretical amount was actually obtained; there is no doubt that a large proportion of the nascent carbon monoxide produced by the dissociation of the dimolecular product, $OC : CO \rightleftharpoons 2OC <$ first formed in the oxidation unites at once with the oxygen present to give carbon dioxide. Nef observed that much carbon dioxide, as well as carbon monoxide, is formed in the burning of bromacetylidene in aqueous

solution, by oxygen.¹ In order, therefore, to have an exact determination of the percentage of oxidation of dibromacetylidene which takes place according to the equation,



it is obviously necessary to determine also the proportion of the carbon monoxide which has been oxidized to carbon dioxide. This would easily have been possible by means of a separate quantitative experiment in a nitrogen atmosphere, but as the large amount of perbromethylene obtained at the end of the oxidation, as well as the other data, also establish the point pretty accurately, proving that about 78.4 per cent proceeds according to the equation given, an exact determination was deemed unnecessary. An investigation of the products present in the alcoholic solution after oxidation was carried out as follows: Much water was added, and the oils separating out were extracted with ether; the ethereal solution was then washed well with water. The water solution contained a large amount of hydrobromic acid and traces of oxalic acid. The ether was removed, after drying with calcium chloride, by means of a Glinsky apparatus, and the oils left behind were fractionated (16 mm.). The following fractions were obtained: I. 8.9 grams, b. p. 55°–73; II. 8.5 grams, b. p. 81°–90°; III. 2.3 grams, b. p. 95°–110°, which solidified at once on cooling and consisted of practically pure perbromethylene. Fractions I. and II. were treated separately, at –10°, with 25 cc. and 45 cc. of 10 per cent ammonia; 0.15 and 0.8 gram of oxamide, respectively, with all its characteristic properties, were obtained.

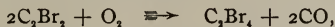
0.5551 gram substance gave 0.2134 gram NH_3 (Kjeldahl).

	Calculated for (CONH_2) ₂ .	Found.
N	31.81	31.68

On spontaneous evaporation of the aqueous ammoniacal solutions used in the experiments just mentioned, and subsequent digestion of the salt residue with benzene, 1 gram of pure dibromacetamide, m. p. 156°, was obtained. The oils

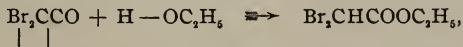
¹ Ann. Chem. (Liebig), 298, 358.

left insoluble and unaffected by the treatment with ammonia, fractions I. and II., were combined and, on distillation (15 mm.), 7.3 grams of oil, b. p. 65° – 75° , or b. p. 163° – 167° , under ordinary pressure, were obtained which was proved to consist chiefly of tribromomethylene containing small amounts of unsymmetrical dibromovinyl ethyl ether. In addition, 3.4 grams more of pure perbromomethylene were obtained, which makes the total amount of pure perbromomethylene, m. p. 55° – 56° , 5.7 grams. On the assumption that the 14 grams of dibromacetylidene present at the beginning of the experiment burned completely according to the equation



13.1 grams of perbromomethylene must result. On the basis that 78.4 per cent of the reaction proceeds in this manner, 10.1 grams of perbromomethylene must be formed; the amount actually obtained, 5.7 grams, is necessarily low because of the difficulty of separating sharply a mixture of tribromomethylene and tetrabromomethylene; furthermore, it is quite probable that a portion of the bromine set free also reacts with the large excess of alcohol present to give HBr, etc., and the hydrogen bromide formed may then, in part, give tribromomethylene with the dibromacetylidene present. How are we, however, to explain the formation of the oxalic and dibromacetic acids? Obviously, as follows:

A. Dibromacetylidene, in taking up oxygen, first gives dibromacetylidene oxide, $\text{Br}_2\text{C} : \text{CO}$, and this substance must then, in part, 6.06 per cent by calculation from the above results, add 1 molecule of alcohol,



giving ethyl dibromacetate, which, on treatment with aqueous ammonia, then gives the dibromacetamide obtained in the experiment.

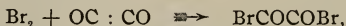
B. Dibromacetylidene oxide, however, being dissociated according to



burns mainly to dimolecular carbon monoxide, $\text{OC} : \text{CO}$, which, in great part, spontaneously dissociates, giving monomolecular carbonic oxide, or unites with more oxygen to give carbon dioxide. The bromine which falls off from dibromacetylidene oxide is, in turn, mainly taken up by unchanged dibromacetylidene,



giving tetrabromethylene; a small percentage, 15.54 per cent by calculation from the data given above, of the bromine must, however, unite with the dimolecular carbon monoxide, $\text{OC} : \text{CO}$, to give oxalyl bromide,



which at once gives, with the alcohol present, hydrogen bromide and ethyl oxalate; the latter then gives, with ammonia, the oxamide obtained in the experiment.

The experiment described above shows, therefore, that dibromacetylidene, in alcoholic solution, unites with dry oxygen according to the following three equations:

- I. Main reaction, 78.4 per cent, $2\text{Br}_2\text{C}_2 + \text{O}_2 \rightleftharpoons \text{Br}_4\text{C}_2 + 2\text{CO}$ (including CO_2);
- II. 15.54 per cent, $\text{Br}_2\text{C}_2 + \text{O}_2 \rightleftharpoons \text{BrCOCOCBr}$;
- III- 6.06 per cent, $2\text{Br}_2\text{C}_2 + \text{O}_2 + 2\text{H} - \text{OC}_2\text{H}_5 \rightleftharpoons 2\text{Br}_2\text{CHCOOC}_2\text{H}_5$.

Dibromacetylidene Diiodide and Diiodacetylidene Dibromide are Identical.

As mentioned above, Lemoult's dibromacetylidene diiodide was isolated in large amount because it was especially well adapted for the quantitative estimation of dibromacetylidene. The yellowish substance crystallizes from hot alcohol in large, flat, transparent needles and separates out almost completely. The identity with Nef's diiodacetylidene dibromide¹ was proved by a careful comparison of the two products as regards crystalline form, solubility, etc. Furthermore, the product analyzed by Nef in 1896, when mixed with an equal

¹ Ann. Chem. (Liebig), 298, 354.

amount of dibromacetylidene diiodide, melted sharply at 95° , so that there can be no possible doubt as to the identity of the products. It follows, therefore, that diiodacetylidene must possess the constitution represented by the formula $I_2C:C$; and since bromacetylidene diiodide is converted smoothly, by means of alcoholic potassium hydroxide, sodium phenolate, or potassium acetate into bromide and diiodacetylidene,¹ the acetylidene formula is definitely established also in the case of the monohalogenated acetylidenes.

Phenyl dibromvinyl Ether, $Br_2C:CHOC_6H_5$, from Tribromethylene and from Unsymmetrical Dibromiodethylene.

Sabanejeff² found that on treating tribromethylene with alcoholic potassium phenolate, dibromvinyl phenyl ether, m. p. 38° , is formed in small quantity. Nef,³ in repeating this experiment with alcoholic sodium phenolate, under definite conditions, obtained a very large yield of the substance and observed that it boils, without decomposition, at 143° (25 mm.). In repeating the experiment according to Nef's directions, I have obtained an 82 per cent yield of the pure product. The same substance is formed, furthermore, on treating the unsymmetrical dibromiodethylene, $Br_2C:CHI$, described above, with alcoholic sodium phenolate; this at once leads to the conclusion that the substance must possess the unsymmetrical formula, $Br_2C:CHOC_6H_5$, given to it by Nef. The correctness of this deduction was finally established beyond doubt by the quantitative conversion of dibromvinyl phenyl ether, by means of nitric acid, at -10° , into nitrated phenyl dibromacetate, etc.,



Finally, it is clear, as was pointed out by Nef in 1897, and as has since been confirmed in many instances by his work on the alkyl haloids,⁴ that the interaction between tribromethylene or dibromiodethylene and alcoholic sodium or potassium phenolate must be interpreted as follows: The halogenated ethyl-

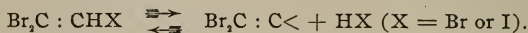
¹ Ann. Chem. (Liebig), 298, 359.

² Ibid., 216, 283.

³ Ibid., 298, 360 (foot-note).

⁴ Ibid., 298, 359; 309, 126; 318, 1.

enes do not react as such, but because they are partially dissociated, at ordinary temperatures, according to the equation



The metallic phenolate, therefore, is acted upon by the halogen acid present, giving metallic haloid and free phenol, $\text{H}-\text{OC}_6\text{H}_5$, which *may or may not*, depending *entirely* on the speed of the reaction, be added to the *other* dissociation product, $\text{Br}_2\text{C} : \text{C} <$, present, to give phenyl dibromvinyl ether, $\text{Br}_2\text{C} : \text{CHOC}_6\text{H}_5$. If the reaction proceeds too rapidly the active dibromacetylidene molecules, not finding enough dissociated phenol molecules present, go over, mainly, into the comparatively inert dibromacetylidene,



which, as was proved by special experiments, when once formed, does not absorb phenol to any extent. The correctness of these conclusions was repeatedly confirmed in my experiments with tribromomethylene and alcoholic sodium phenolate; thus, if one heats, rapidly, a mixture of molecular quantities of tribromomethylene and sodium phenolate, much free dibromacetylidene and carbolic acid are formed and correspondingly smaller amounts of phenyl dibromvinyl ether; it is, in fact, impossible to prevent entirely the formation of dibromacetylidene in the experiment, but the following method gives always an 82 per cent yield of phenyl dibromvinyl ether.

An alcoholic solution containing sodium ethylate, from 4.3 grams of sodium, was slowly added, by means of a dropping funnel, to a solution containing 25 grams of tribromomethylene, 19 grams of phenol and 25 cc. of alcohol. During the operation and for 12 hours afterwards the temperature was kept at 0° . Finally, the mixture was heated slowly to 100° and kept for 4 hours at that temperature to complete the reaction. On pouring into much water, extracting with ether, washing the ether solution with sodium hydroxide, then with water and drying with calcium chloride, 21.4 grams of phenyl dibromvinyl ether, a sweet smelling oil, boiling at 142° (25 mm.)

were obtained. The substance melts at 38° – 39° and has sp. gr. 1.799 at 25° (Westphal).

0.4752 gram substance gave 0.6450 gram AgBr (Carius).

	Calculated for $C_8H_6OBr_2$.	Found.
Br	57.56	57.74

A fair yield of the same product was also obtained from dibromiodethylene by means of alcoholic sodium phenolate. Fifty cc. of an alcoholic solution containing sodium ethylate, from 4.3 grams of sodium, were slowly added to a cold solution of 28 grams of dibromiodethylene, b. p. 91° (15 mm.), 17 grams of phenol and 15 grams of alcohol; the mixture was allowed to stand at 0° for 17 hours and then gradually heated to 95° and kept at that temperature for 2 hours. On working up, as in the case just mentioned, 12.8 grams of phenyl dibromvinyl ether, b. p. 135° – 140° (15 mm.), 52 per cent of the theoretical amount, were obtained. The oil solidified at once on cooling and the crystals, when mixed with an equal quantity of the corresponding substance from tribromethylene, melted unchanged at 38° – 39° .

On the Conversion of Phenyl dibromvinyl Ether into Dibromacetamide.

Ten grams of phenyl dibromvinyl ether were added, drop by drop, to 30 cc. of fuming nitric acid at -10° ; a hissing noise, with decided heat evolution, was noticed and the yellowish precipitate first formed dissolved subsequently on shaking. The mixture was left standing at room temperature for 2 days and then poured on ice. The oil which separated out was extracted with ether and washed with small amounts of water; after removing the ether it was mixed with 3 cc. of concentrated sulphuric acid and 20 cc. of absolute alcohol and kept for 3 hours¹ at 100° . On adding water, an oil, possessing a sharp odor and causing tears, was precipitated. This was treated with 75 cc. of 15 per cent aqueous ammonia, at -10° . The crystals which came out were collected and the residue obtained after the spontaneous evaporation of the ammoniacal solution was extracted with benzene. Thus a total of 4 grams

¹ E. Fischer: Ber. d. chem. Ges., 28, 3252.

of pure dibromacetamide, m. p. 155° – 156° , were obtained which is 51.3 per cent of the amount theoretically possible.

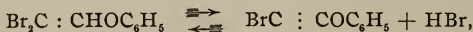
0.1468 gram substance gave 0.2543 gram AgBr (Carius).

	Calculated for $C_2H_5Br_2NO$.	Found.
Br	73.73	73.71

On the Conversion of Phenyl dibromvinyl Ether into Bromacetic Acid.

Nef has shown that the analogous ethyl dibromvinyl ether, $Br_2C:CHOC_2H_5$, is converted, quantitatively, by fuming nitric acid into ethyl dibromacetate.¹ On treatment with alcoholic potassium hydroxide, on the other hand, this substance first gives ethyl bromacetate; consequently, Nef concluded that in this reaction, as well as in the analogous one with diiodoacetylidene,² ethoxy halogen acetylene, $XC:COC_2H_5$, must first be formed which, however, being too reactive, at once absorbs the alcohol or water present, giving ethyl halogen orthoacetate, $XCH_2C(OC_2H_5)_3$, or ethyl halogen acetate, $XCH_2COOC_2H_5$. Slimmer has since obtained similar results with alcoholic potassium hydroxide on the phenyl dibromvinyl ether of Sabanejeff and Nef.³ I have, therefore, continued to study the behavior of phenyl dibromvinyl ether towards various reagents, especially in the hope of being able to obtain direct proof of the intermediate formation of bromphenoxyacetylene.

Phenyl dibromvinyl ether is remarkable on account of the ease with which it loses one of its halogen atoms. Thus it loses 1 molecule of hydrogen bromide on heating to 100° for a short time, in the presence of alcohol, water, or acetic acid; the other product formed, besides phenol, is invariably bromacetic acid or its ester. The only rational interpretation of these facts is the one given by Nef, namely, that phenyl dibromvinyl ether is dissociated according to the equation



¹ Ann. Chem. (Liebig), **298**, 335.

² *Ibid.*, **298**, 337, 349.

³ Ber. d. chem. Ges., **36**, 289.

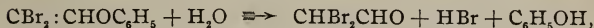
and that the bromphenoxyacetylene at once absorbs water, etc., giving phenol and bromacetic acid, thus :



In view of all this I made many attempts to isolate bromphenoxyacetylene, by treating phenyl dibromvinyl ether with alcoholic potassium hydroxide, powdered potassium hydroxide, aniline, quinoline, pyridine, etc., but always without success.

It should be pointed out here that the bromphenoxyacetylene mentioned by Sabanejeff¹ has been proved by Slimmer not to exist² and I have confirmed the results obtained by the latter.

Finally, I give a brief summary of my results obtained while studying the action of water, alcohol and acetic acid on phenyl dibromvinyl ether. It was hoped, at first, that in this way dibromacetaldehyde and phenol might be formed, according to the equation :



but not a trace of the former substance, whose properties were carefully studied, could be found ; furthermore, it cannot have been formed as an intermediate product because special experiments with dibromacetaldehyde prove that it remains unchanged by treatment with the above named reagents.

Ten grams of phenyl dibromvinyl ether, 2 grams of water and 0.2 gram of phenol were heated in a sealed tube, for 4 hours, at 100°. On adding water, extracting with ether, washing with sodium carbonate, etc., 3.1 grams of bromacetic acid, b. p. 110° (22 mm.) and crystallizing on cooling, were obtained, theory = 4.1 grams. The part neutral to sodium carbonate was found to consist of 3 grams of phenol, b. p. 88° (22 mm.), theory = 3.3 grams. Eight grams of phenyl dibromvinyl ether and 20 cc. of absolute alcohol were heated in a sealed tube, at 100°, for 6.5 hours. Besides hydrogen bromide, 2.5 grams of phenol, b. p. 87° (25 mm.) and 4.8 grams of ethyl bromacetate, b. p. 156°, were obtained ; the latter gave, on treatment with aqueous ammonia, bromacetamide.

¹ Ann. Chem. (Liebig), 216, 282.

² Loc. cit.

Ten grams of phenyl dibromvinyl ether and 8 grams of glacial acetic acid were heated in a sealed tube, for 5 hours, at 100°. There were obtained 5.7 grams of phenyl bromacetate,¹ b. p. 140 (20 mm.), m. p. 32°.

0.2458 gram substance gave 0.2070 gram AgBr (Carius).

	Calculated for C ₈ H ₇ O ₂ Br.	Found.
Br	37.21	35.83

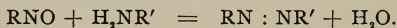
In conclusion, I wish to express my thanks and gratitude to Professor Nef for the inspiration and help which he has given me in this work.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XI.—THE CONDENSATION OF THE THREE NITRANILINES WITH *p*-NITROSOBENZALDEHYDE.

BY FREDERICK J. ALWAY AND ROSS A. GORTNER.

Under favorable conditions many nitroso compounds react almost quantitatively with amino compounds to produce azo derivatives, according to the equation :



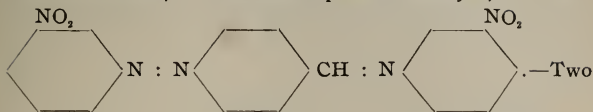
We have found that *p*-nitrosobenzaldehyde condenses readily with *m*-nitraniiline, less readily with *p*-nitraniiline and with so much difficulty with *o*-nitraniiline that we were unable to isolate any of the condensation product.

The readiness with which the nitraniilines condense with *p*-nitrosobenzaldehyde varies as their basicity. In regard to the latter property Kleemann² has shown that, when equal weights of the three hydrochlorides are boiled with the same volume of water for a short time, and then evaporated to dryness at 75°, there is decomposed into base and hydrochloric acid; of the

<i>o</i> -nitraniiline hydrochloride	63.8 per cent
<i>p</i> - " " "	13.1 " "
<i>m</i> - " " "	3.4 " "

¹ Kunckell and Scheven : Ber. d. chem. Ges., 31, 172.

² Ibid., 19, 336 (1886).

m-Nitranilide of *m*-Nitrobenzene-*p*-azobenzaldehyde,

grams of *p*-nitrosobenzaldehyde, dissolved in 25 cc. of glacial acetic acid, were slowly added to a boiling acetic acid solution of 5 grams of *m*-nitraniline. The mixture became deep red in color and, after being kept near the boiling point for a few minutes, was allowed to cool slowly. Brick red, granular masses separated out. These were washed on the filter with 95 per cent alcohol and dried at 110°.

0.1756 gram substance gave 31.3 cc. moist N at 25° and 727 mm.

	Calculated for $C_{19}H_{13}O_4N_5$.	Found.
N	18.66	19.00

The compound melts at 239°.5 (corr.), is readily soluble in nitrobenzene but only sparingly soluble in ethyl alcohol, amyl alcohol and glacial acetic acid. It is only partly decomposed by cold, dilute nitric acid. By prolonged treatment with hot, dilute hydrochloric acid it is entirely resolved into *m*-nitrobenzene-*p*-azobenzaldehyde and *m*-nitraniline.

We obtained the same compound by the condensation of *m*-nitrobenzene-*p*-azobenzaldehyde with *m*-nitraniline, using glacial acetic acid as a solvent for both the reacting compounds.

m-Nitrobenzene-*p*-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CHO$.—We have found that the substance to which this name was previously ascribed¹ consists largely of the condensation product described above, the decomposition of the latter by cold, dilute nitric acid having been incomplete.

The anilide, melting at 239°.5, was placed in a flask covered with dilute hydrochloric acid, 13 per cent, and kept at 60° to 80° for 1 hour. The resulting mixture was treated with cold

¹ THIS JOURNAL, 32, 398 (1904).

water and filtered. The residue was thoroughly washed with cold water, dried and recrystallized from dilute ethyl alcohol.

0.1849 gram substance gave 28.1 cc. moist N at 23° and 724 mm.

0.2348 gram substance gave 0.5241 gram CO₂ and 0.0173 gram H₂O.

	Calculated for C ₁₃ H ₉ O ₃ N ₃ .	Found.
C	61.2	60.9
H	3.5	3.4
N	16.5	16.3

This aldehyde forms minute, red needles melting at 135° (corr.). It is very soluble in ethyl alcohol, amyl alcohol, glacial acetic acid and nitrobenzene; fairly soluble in benzene, toluene, chloroform, ethyl acetate and acetone; and difficultly soluble in ether, methyl alcohol, ligroin and carbon bisulphide.

Phenylhydrazone of m-Nitrobenzene-p-azobenzaldehyde,
O₂NC₆H₄N : NC₆H₄CH : NNHC₆H₅.—A solution of *m*-nitrobenzene-*p*-azobenzaldehyde in 95 per cent alcohol was treated with an excess of phenylhydrazine and heated on the water-bath for 1 hour. After the heating had been continued for some time crystals began to separate from the dark red solution. The crystals were washed on the filter with alcohol and dried at 100°.

0.1234 gram substance gave 23.6 cc. moist N at 25° and 724 mm.

	Calculated for C ₁₉ H ₁₅ O ₂ N ₅ .	Found.
N	20.3	20.3

This hydrazone forms dark red, rectangular plates, melting at 213°.5 (corr.).

Oxime of m-Nitrobenzene-p-azobenzaldehyde,
O₂NC₆H₄N : NC₆H₄CH : NOH.—A solution of 0.7 gram of sodium hydroxide, in water, was treated with 0.4 gram of hydroxylamine hydrochloride, then with an alcoholic solution of 1 gram of *m*-nitrobenzene-*p*-azobenzaldehyde and finally heated for 1.5 hours on the water-bath. The red solution, so

obtained, was treated with water and acidified with acetic acid. The precipitate was filtered out, washed with water and recrystallized from dilute alcohol.

0.1817 gram substance gave 35.2 cc. moist N at 25° and 724 mm.

	Calculated for $C_{13}H_{10}O_2N_4$.	Found.
N	20.7	20.6

The oxime forms yellow crystals, melting at 116° (corr.).

Anilide of m-Nitrobenzene-p-azobenzaldehyde,

$O_2NC_6H_4N : NC_6H_4CH : NC_6H_5$.—A mixture of *m*-nitrobenzene-*p*-azobenzaldehyde with an excess of aniline was heated 1 hour at 110°, cooled and treated with absolute alcohol, which precipitated the anilide. The latter was filtered out, washed with alcohol, dried, dissolved in hot benzene and reprecipitated by the addition of absolute alcohol.

0.1383 gram substance gave 22.7 cc. moist N at 27° and 724 mm.

	Calculated for $C_{19}H_{14}O_2N_4$.	Found.
N	17.0	17.2

This compound forms small, yellow crystals, melting at 132° (corr.).

p-Nitranilide of p-Nitrobenzene-p-azobenzaldehyde,



—Six grams of *p*-nitrosobenzaldehyde, dissolved in hot, glacial acetic acid, were slowly added to a boiling solution of 15 grams of *p*-nitraniline in glacial acetic acid. The mixture was heated a few minutes and then allowed to cool slowly. A dark red, granular mass separated from the brownish-red solution on cooling. This was filtered out, washed on the filter with alcohol and recrystallized from glacial acetic acid. The crystals were washed on the filter with hot alcohol and dried.

0.2672 gram substance gave 44.5 cc. moist N at 20° and 734 mm.

	Calculated for $C_{19}H_{18}O_4N_6$.	Found.
N	18.7	18.4

This compound forms small, red needles, melting at 237°–238°.5 (corr.); it is sparingly soluble in alcohol but readily soluble in hot, glacial acetic acid.

p-Nitrobenzene *p*-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CHO$.—The anilide, melting at 237°–238°.5, was treated with dilute hydrochloric acid, 3 parts of concentrated acid to 1 part of water. The mixture was kept at 60° for 2 hours and was then filtered, washed on the filter with hot, dilute hydrochloric acid and, finally, with alcohol. The crude product, so obtained, was recrystallized from glacial acetic acid.

I. 0.1348 gram substance gave 19.8 cc. moist N at 10° and 728 mm.

II. 0.2032 gram substance gave 0.4541 gram CO_2 and 0.0820 gram H_2O .

III. 0.1768 gram substance gave 0.3970 gram CO_2 and 0.0570 gram H_2O .

	Calculated for $C_{19}H_{18}O_4N_6$.	I.	Found. II.	III.
C	61.2	. .	60.9	61.3
H	3.5	. .	4.0	3.5
N	16.5	16.8	. .	. .

p-Nitrobenzene-*p*-azobenzaldehyde crystallizes in long, red plates, melting at 221°–222° (corr.). It is very soluble in hot benzene, glacial acetic acid, nitrobenzene and amyl alcohol, and moderately soluble in each of these solvents in the cold. It is fairly soluble in acetone, chloroform and ethyl acetate, and sparingly soluble in ethyl alcohol, methyl alcohol, ether, ligroin and carbon bisulphide.

Anilide of p-Nitrobenzene-*p*-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CH:NC_6H_5$.—A mixture of *p*-nitrobenzene-*p*-azobenzaldehyde with an excess of aniline was heated to 110°, for 2 minutes and then cooled. The solid substance thus obtained was dried on a porous plate and recrystallized

from benzene. In the preparation of this compound it is important that the heating be discontinued at the end of 2 minutes as, otherwise, the anilide seems to undergo decomposition.

0.1392 gram substance gave 21.3 cc. moist N at 20° and 724 mm.

	Calculated for $C_{19}H_{14}O_2N_4$.	Found.
N	17.0	16.7

This anilide forms stellate groups of orange-colored needles, melting at 152° (corr.) and is insoluble in absolute alcohol.

Oxime of p-Nitrobenzene-p-azobenzaldehyde,
 $O_2NC_6H_4N : NC_6H_4CH : NOH$.—A solution of 1 gram of sodium hydroxide in water was treated with 0.6 gram of hydroxylamine hydrochloride, then with an alcoholic solution of 1.5 grams of *p*-nitrobenzene-*p*-azobenzaldehyde and, lastly, was heated to boiling for 3 hours. The reaction product was treated with water and acetic acid and filtered. The residue was washed with alcohol and dried at 100°.

0.0986 gram substance gave 17.8 cc. moist N at 17° and 736 mm.

	Calculated for $C_{18}H_{10}O_2N_4$.	Found.
N	20.7	20.3

This oxime forms a yellow solid not melting below 290°.

We failed to obtain the phenylhydrazone of *p*-nitrobenzene-*p*-azobenzaldehyde in a pure condition.

Condensation of o-Nitraniline with p-Nitrosobenzaldehyde.—We tried to effect the condensation by the method that had succeeded in the case of *m*-nitraniline and *p*-nitraniline. The acetic acid solution became red, indicating the formation of some azo compound. However, even after 3 hours' heating, at the boiling point of acetic acid, with an excess of *o*-nitraniline, a large amount of unchanged *p*-nitrosobenzaldehyde remained, as we were able to demonstrate by distillation with steam. From the small amount of residue after the treatment with steam we were unable to isolate any condensation product.

VARIABLE SENSITIVENESS IN COLORIMETRY. III.

BY DAVID W. HORN AND SUE A. BLAKE.

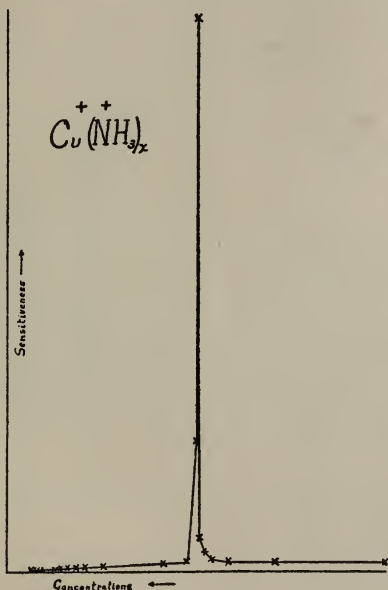
In extending the investigation of the relation between sensitiveness and concentration in colorimetry, we have studied ammoniacal solutions of copper sulphate. The results of this study and a graph based upon them are given below. The same phenomena are to be observed here as in the cases previously described. A constant fraction and a constant ratio characterize our measurements in these solutions as they did in solutions of copper sulphate in water. The remarkable increase and the subsequent rapid decrease in sensitiveness that occur near the maximum of sensitiveness have been studied more closely in this case than heretofore, with the result that the maximum of sensitiveness appears to be even more accentuated than we have previously indicated.

The experimental results follow :

Table I.—Ammoniacal Solutions of Copper Sulphate.

Number of experiment.	Concentration stated as liters that contain one gram atom of Cu.	Milligrams of Cu producing a just perceptible difference in color in 50 cc.	Sensitiveness: reciprocals of values found in column 3.	$\frac{\sqrt{V}}{14}$.	$\frac{S}{85}$.
1.	2.	3.	4.	5.	6.
1	83.6	1.905	0.52	0.65	0.006
2	100.0	2.220	0.45	0.71	0.005
3	125.2	1.651	0.61	0.80	0.007
4	166.8	1.016	0.98	0.92	0.012
5	277.7	0.7314	1.37	1.19	0.016
6	333.3	0.5724	1.75	1.31	0.020
7	384.6	0.4452	2.25	1.40	0.026
8	500.0	0.3180	3.14	1.60	0.037
9	666.6	0.2385	4.19	1.83	0.049
10	799.9	0.1987	5.03	2.02	0.059
11	1250.0	0.1272	7.86	2.53	0.092
12	3333.3	0.0636	15.72	4.13	0.185
13	4443.9	0.0530	18.87	4.76	0.222
14	4966.9	0.0034	294.12	5.03	3.46
15	4996.1	0.0008	1250.00	5.04	14.71
16	5000.0	0.0132	75.75	5.05	0.89
17	5332.7	0.0265	37.87	5.21	0.44
18	5714.3	0.0397	25.25	5.40	0.29
19	6666.6	0.0795	18.94	5.83	0.21
20	10000.0	0.0795	18.94	7.14	0.22
21	20000.0	0.0795	18.94	10.10	0.22

The results in Table I., when plotted, give the following graph, in which the ordinates are proportional to the square roots of the sensitiveness and the abscissae to the concentrations:



The results in Table I. are amplified in Table II. to show :

1. The ratio between the amount of copper that just suffices to produce an appreciable difference in color in 50 cc. of each solution and the total amount of copper present in 50 cc. of the solution at the different concentrations studied. This ratio is represented in the table by Δ/β' . This value Δ/β' multiplied by 100, gives directly the percentage error inherent in the comparisons of the color.

2. The ratio between the total amounts of copper in two 50 cc. tubes containing solutions that exhibit the minimum perceptible difference in color. This ratio is represented in the table by β/β' .

In Table II. the experiments are numbered and given in the same order as in Table I. :

Table II.—Ammoniacal Solutions of Copper Sulphate.

Number of experiment.	Milligrams Cu : total in 50 cc. of solution. β .	Milligrams Cu producing just perceptible color in 50 cc. Δ .	$\beta' = \beta + \Delta$.	Δ/β' .	Variation from mean in experiments 1-13, inclusive.	β/β' .	Variation from mean in experiments 1-13, inclusive.
1.	2.	3.	4.	5.	6.	7.	8.
1	38.100	1.905	40.005	0.05	—0.006	0.95	+0.005
2	31.750	2.220	33.970	0.07	+0.014	0.94	—0.005
3	25.400	1.651	27.051	0.06	+0.004	0.94	—0.005
4	19.050	1.016	20.066	0.05	—0.006	0.95	+0.005
5	11.448	0.7314	12.1794	0.06	+0.004	0.94	—0.005
6	9.540	0.5724	10.1124	0.06	+0.004	0.94	—0.005
7	8.268	0.4452	8.7132	0.05	—0.006	0.95	+0.005
8	6.360	0.3180	6.6780	0.05	—0.006	0.95	+0.005
9	4.770	0.2385	5.0085	0.05	—0.006	0.95	+0.005
10	3.975	0.1987	4.1737	0.05	—0.006	0.95	+0.005
11	2.544	0.1272	2.6712	0.05	—0.006	0.95	+0.005
12	0.954	0.0636	1.0176	0.06	+0.004	0.94	—0.005
13	0.716	0.0530	0.7690	0.07	+0.104	0.93	—0.015
14	0.640	0.0034	0.6434	0.005			
15	0.637	0.0008	0.6378	0.001			
16	0.636	0.0132	0.6492	0.02			
17	0.596	0.0265	0.6225	0.04			
18	0.556	0.0397	0.5957	0.07			
19	0.477	0.0795	0.5565	0.14			
20	0.318	0.0795	0.3975	0.20			
21	0.159	0.0795	0.2385	0.33			

One of the most interesting points that appears when these tables are compared with those in the preceding paper is the close agreement in the values for the ratio β/β' for the copper-blue and the cuprammonium-purple. In the one case the average value is 0.92 and in the other 0.94. There is a sug-

gestion in this of the possibility that the ratio β/β' is a constant that is independent of the color examined. This can be tested by the study of the compounds of the same element that have different colors in solution. Data involving different elements are at present not comparable, for the term "gram-atomic color" has no significance that is known, nor is any idea analogous to the one it would express generally accepted.

The concordance in the data obtained up to the present in this investigation, considered along with the satisfactory character of the interpretation of these data in terms of "the *fundamental* psycho-physical law"—Weber's Law—make it very probable that the following generalizations apply to colorimetric analysis as a whole :

Equal weights of colored solute do not produce equal differences in color *except* when they are added to colored solutions whose concentrations are equal. For example, only 0.00027 as much potassium chromate must be added to a 0.000125 N solution of chromate to change its color perceptibly as must be added to a 0.004 N solution to produce a perceptible effect ; and about 13 times as much chromate must be added to distilled water to give the water a visible color as must be added to a 0.000125 N solution of chromate to change its color perceptibly.

The weight of colored solute required to produce a just perceptible difference in color when added to a colored solution varies greatly with the concentration of the colored solution, and varies in a very irregular way, but the general behavior is the same in all cases and is independent of the color under examination. This may be seen in the forms of the graphs for CrO_4^{--} , Cu^{++} and $\text{Cu}(\text{NH}_3)_x^{++}$.

The whole range of concentrations from those of solutions too deeply colored for use, to those of solutions too feebly colored to be distinguishable from distilled water exhibits 3 different and characteristic sets of relations between sensitiveness and concentration. For clearness, these 3 parts of the total range will be dealt with separately.

The first begins with the most concentrated solutions that

can be used in colorimetry and includes a large number of lesser concentrations, at any one of which the relation between sensitiveness and concentration is expressed by the law that *the sensitiveness varies inversely as the concentration, or, the product of the sensitiveness into the total weight of colored solute present is a constant*. This law may be stated in other forms so that the sensitiveness—a term defined arbitrarily in the first paper of this series—does not enter into consideration. Thus, *the weight of colored solute that must be added to a colored solution to produce a just perceptible difference in color is a constant fraction of the total weight of colored solute present*; in this form there is an example of the law to be found in column 5, Table II. Another statement is that *the weights of colored solute in any 2 solutions that are just distinguishable by color bear a constant ratio to each other*, and an example of the law in this form may be found in column 7, Table II. It has been shown in the preceding paper that throughout the range in which the above law is valid, the percentage error arising from the limitation of the eye in the matching of colors is constant and independent of the concentrations of the solutions compared.

The second begins where the above law ceases to be valid. From this point on the weight of colored solute required to produce a perceptible difference in color becomes rapidly a smaller and smaller fraction of the total weight of colored solute present, attains and passes through a minimum limiting value, and then rapidly becomes a larger and larger fraction of the total weight of colored solute present. For example, in ammoniacal solutions of copper sulphate the fraction within the first part of the range of concentrations has a constant value of about 0.055, whereas in the second it rapidly reaches a value of 0.001 and then rises suddenly to a value of 0.02. At the concentration corresponding to the minimum value of the fraction the percentage error in the estimation of color will have but about 0.018, the value that it had in the first part of the range. It is within this *second* part that all colorimetric analyses should be made. The nearer the concentrations of the solutions in the analyses are to those corresponding to the minimum value of the fraction, *i. e.*, to the maximum sensi-

tiveness, the less the necessary percentage error due to the eye in the estimation of the colors.

The third range may be considered as commencing where the fraction just mentioned acquires a value greater than it had in the first. This third part includes solutions that are very faintly colored. The eye is unable, finally, to distinguish the solutions from distilled water. Usually the percentage error is considerably greater in this third range than elsewhere, so that solutions having these concentrations should be avoided in colorimetric analysis.

It seems to us that data such as we have represented by the curve of sensitiveness must be known in each colorimetric method if the method is to be used to greatest advantage and the results are not to be affected by errors of unknown magnitudes. When such data have been accumulated for the several important methods it will be possible, by a comparison of these data, to establish the relative merits of different colorimetric methods that have been suggested for the same purposes. In the absence of these data, colorimetric analysis lacks an exact and satisfactory basis.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June, 1906.

OBITUARY.

WILHELM MEYERHOFFER.

Professor Wilhelm Meyerhoffer was born at Pinsk, Russia, September 13, 1864, and died April 21, 1906. His education was obtained at Czernowitz, Heidelberg and Strassburg. He received the Ph.D. from the University of Amsterdam, in 1889, his research, an investigation of cupribipotassium chloride, being carried out under the direction of Professor van 't Hoff. After brief residences in Vienna, Paris and Leipzig he returned to van 't Hoff, with whom he has ever since been closely associated. In addition to his title of professor, he has been for many years a "Privatdozent" of the University of Berlin.

Meyerhoffer is best known for his investigations of heterogeneous equilibria and his work, with van 't Hoff, on the formation of the Stassfurt salt beds. In 1892 he published a text-book on Stereochemistry, followed, in 1893, by an ad-

mirable volume on the "phase rule;" he was also chiefly responsible for the publication of the last (5th) edition of Landolt-Börnstein's "Physikalisch-Chemische Tabellen," in 1905.

REVIEWS.

PETROGENESIS. Von C. DOELTER, o. Professor der Mineralogie und Petrographie an der Universität Gratz. Die Wissenschaft. Sammlung naturwiss. u. math. Monographien. Heft 13. Braunschweig: Vieweg und Sohn. 1906. Price, M. 7, geb. M. 7.80.

This little volume, forming the thirteenth monograph in the series issued by F. Vieweg and Son, maintains the high standard of excellence shown by previous issues. It is a timely resumé of the large amount of work which has appeared in recent years on the Origin of Rocks. The present book is based more largely on experimental work on the formation of minerals and rocks than has been the case heretofore. The 14 chapters, with the brief subject and author indices, permit one to gain ready access to the latest views regarding the mode of origin of the different kinds of rock constituting the earth's crust.

The first half of the discussion is devoted to igneous rocks and includes a digest of the modern investigations regarding vulcanism and the interior of the earth, the external features and structure of eruptive rocks, the chemical peculiarities of rocks and the causes producing them, and the artificial production of known rocks. The latter half is given to a consideration of the metamorphic and sedimentary rocks and to chemical precipitates.

The discussions in each case are timely and well proportioned, and give the views of the various investigators. It is a matter of regret, however, that these views have not been more thoroughly digested and the results generalized in summary paragraphs. The treatment throughout is from the chemico-physical standpoint, rather than the geological. The book is not a text-book of petrography, but an attempt to bring together such facts and theories as may aid in explaining why rocks are as we find them. The style is clear and the statements concise, but the demand on the knowledge of the reader is great. There is, however, no other book which so clearly outlines the attempts which are now being made to apply physico-chemical laws to the complex problems presented by the reactions taking place in the solid crust of the earth.

E. B. M.

LES NOUVEAUTÉS CHIMIQUES POUR 1906. Nouveaux Appareils de Laboratoire, Méthodes nouvelles de Recherches Appliquées à la Science et à l'Industrie, par CAMILLE POULENC, Docteur ès Sciences. Avec 203 Figures intercalées dans le Texte. Paris: J. B. Baillière et Fils. Price, 4 Fr.

This new number of Dr. Poulenc's excellent yearbook includes practically all of the improvements in apparatus made within the last 12 months in France and in Germany. Although the novelties this year are less important than last, the book is worth perusal, as it contains descriptions of many minor improvements.

E. R.

THEORIEN DER CHEMIE. Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. Von SVANTE ARRHENIUS. Mit Unterstützung des Verfassers aus dem englischen Manuskript. Übersetzt von ALEXIS FINKELSTEIN. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1906. pp. 177.

As the title implies, this is the German translation of Arrhenius' lectures at the University of California, during the summer of 1904. In this case, as in most others, the best idea of the ground covered can be gained by a glance at the "contents."

The several chapters deal with "The Uses of Theories; Older Theories in Chemistry—Dalton's law; Discussion of the Validity of the Laws of Dalton; Electrical Forces between Atoms—Faraday's Law; Electrical Forces between Atoms—Chemical Valence and Affinity; The Development of the Conception of Valence; Composition of the Atoms—Electrons; Theory of Gases; Chemical Kinetics and Statics; The Effect of Temperature and Pressure—Dissociation; Osmotic Pressure, General Laws of Dissolved Substances; Electrolytic Dissociation; Unsolved Problems.

It is needless to add that the discussion of these matters is thoroughly up to date, and shows the hand of the master at every turn. This is, of course, just what would be expected from one of the founders of the new school of physical chemistry. As is so well known, it was Arrhenius who, to account for the i in the van't Hoff equation for osmotic pressure, $PV = iRT$, gave the world the theory of electrolytic dissociation—one of the four great generalizations upon which modern physical chemistry rests. The book is comparatively elementary, and should be read by all who are interested in the theories upon which scientific chemistry is based.

H. C. J.

DIE CHEMISCHE REICHSANSTALT. Von WILHELM OSTWALD. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1906. pp. 28.

This little pamphlet by Ostwald is of unusual interest, not only on account of the vivid and fascinating style in which it

is written, but because of the number of important problems which it discusses.

On the 21st of February about 150 persons, interested in scientific and technical chemistry, met in the "Aula" of the University of Berlin to discuss the feasibility of founding a chemical "Reichsanstalt."

In addition to the special problem under consideration, Ostwald discusses in this pamphlet a number of general relations that are of the very highest importance for the development of scientific chemistry. In reference to the possibility of good work being done under unfavorable conditions, says Ostwald, "Es ist ja wahr dass viele grosse Entdeckungen mit sehr bescheidenen Mitteln gemacht worden sind, und dass das Genie eines grossen Mannes glorreich überwinden kann. Aber daneben bleibt doch das Gesetz von der Erhaltung der Energie unerschüttert stehen, und dieses besagt in dem vorliegenden Falle, dass jene grossen Männer noch mehr geleistet hätten, wenn wir den Teil ihrer Energie, den sie zur Überwindung der äusseren Hindernisse zu verbrauchen hätten, unmittelbar auf rein wissenschaftliche Arbeit hätten anwenden dürfen. Die schönen Apparate und Arbeitsräume tun es freilich nicht allein, Sie sind nur ein Faktor in dem Produkt, und das Produkt bleibt Null, wenn der andere Faktor, die Intelligenz des Forschers Null ist. Aber andererseits wächst das Produkt proportional dem Betrag jedes einzelnen Faktors."

Apparently the most prominent figures in this new movement are Professors Emil Fischer and Walter Nernst. The field in which such an institution as that now under consideration is most needed is in analytical chemistry. This institution should make provision for at least the following lines of work: Inorganic chemistry, especially the determination of atomic weights. There should be equipment also for general analytical chemistry, for organic chemistry, and for physical chemistry.

Ostwald pays high tribute to the work of Richards on atomic weights, but this field requires the co-operation of a number of permanent workers. Then the scientific side of metallurgy calls urgently for investigators.

In organic chemistry there is great need of further development in certain directions, especially in the technical applications of organic substances.

In physical chemistry the needs are most pressing. "Diese hat zunächst die wichtigsten Konstanten der reinen Stoffen neu und einheitlich zu bestimmen, d. h. etwa den ganzen Landolt-

Börnstein experimentell neu zu bearbeiten." In addition, the dissociation constants of acids and bases, the solubility of salts, the dielectric constants of organic compounds, should be redetermined. Further, the dynamics of typical reactions, thermochemistry, and especially *catalysis* should be thoroughly investigated. "Die Grundlagen stehen ja fest; eine Unzahl qualitativer Vorgänge im Gebiete der Katalyse sind bekannt, sie brauchen nur systematisch-quantitativ durchgearbeitet zu werden."

The following statement will be of special interest to all Americans: "In der Tat, wenn es ausserhalb Deutschlands ein Land gibt, in welchem die praktische Bedeutung der Wissenschaft klar erkannt wird, so sind es die Vereinigten Staaten."

After discussing the condition of technical affairs, especially in England, Ostwald closes with the significant words: "Darum muss unsere erste und wichtigste Sorge sein, den Plan so schnell als möglich auszuführen. Denn darüber darf man nicht im Zweifel sein; ist eine solche Anstalt einmal vorhanden, so wirkt sie nicht nur katalytisch, sondern auch autokatalytisch, und darum ist für uns Gefahr im Verzuge." H. C. J.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Begründet und bis 1901 herausgegeben von PROF. DR. W. NERNST and PROF. DR. W. BORCHERS.

BERICHTE ÜBER DIE FORTSCHRITTE DES JAHRES 1904. Herausgegeben von DR. PHIL. HEINRICH DANNEEL. XI. Jahrgang. Breslau. Halle a. S.: Verlag von Wilhelm Knapp. 1906. pp. 937. Price, M. 28.

The "Jahrbuch der Elektrochemie" for 1904 differs from the earlier volumes in being, if possible, even more thorough and complete. Rather more space is given to scientific electrochemistry than to applied, the first 556 pages being devoted to the former.

This is easily the most thorough and useful "Jahrbuch" with which the present writer is familiar. The reviews of the various papers are elaborate enough to give a satisfactory conception of their contents, which is more than can be said of many so-called reviews of scientific articles.

One is deeply impressed by the amount of labor that must be expended annually in preparing such a work. It is fair to say that an undertaking of this nature could be carried out successfully only in one country in the world, and that country is Germany.

This "Jahrbuch" will prove of incalculable value to all active workers in the field of electrochemistry, and will be of special use to those who do not have ready access to the original arti-

cles. It will, doubtless, find its way into every scientific library and into every laboratory where scientific work is being done. It is one of the few books upon which only the highest praise can be bestowed.

H. C. J.

LABORATORY MANUAL OF GENERAL CHEMISTRY (Fourth Edition). By THOMAS EVANS and J. F. SNELL. Cincinnati: University Press, University of Cincinnati, Ohio. 1905. pp. 70. Price, \$0.50.

This manual has been written to meet the special needs of students at the University of Cincinnati. The experiments are, in the main, those found in most text-books for students just beginning the study of chemistry; but, as the authors state in the preface, in addition to these certain special experiments have been selected from various books. The choice is good and in most cases the experiments are clearly described, but, of course, such a manual can only be used to advantage in connection with a text-book in which the theory can be followed step by step. The reviewer has found that satisfactory results in quantitative experiments can only be obtained by the beginner under the constant personal supervision of the instructor, and he does not believe that the number of such experiments given in the early part of this book could be followed with advantage to the student except with small classes, or with a greater number of assistants than are usually found in such laboratories. If the chemical course follows a course in physics, where precision and care have been taught, this method might be used; but the first-year chemical courses in colleges are usually taken by those who have had so little training in scientific methods that they do not have the proper conception of the requirements of such work and not enough knowledge of the principles involved to successfully carry out the directions.

J. E. G.

ANLEITUNG ZUM GEBRAUCH DES POLARISATIONSMIKROSKOPS. Von DR. ERNST WEINSCHENK. Freiburg i/B.: Herdersche Verlagshandlung. 1906. Price, \$1.25 net.

This is the second edition of a most useful laboratory book, the first edition of which appeared in 1901. There is no one who can speak with greater authority in regard to the questions pertaining to petrography, or who is better known as a teacher than the author. The present volume contains 147 pages and is enriched with 135 figures and illustrations. The work begins with a discussion of the microscope and its adjustments for use with polarized light. This is followed by chapters on observations with ordinary light, with a parallel beam of polarized light, and with convergent polarized light. After this come the chapter in regard to twinning crystals and

various optical phenomena and an appendix describing in detail various pieces of apparatus.

The work is admirable in every respect and is to be recommended to every student of mineralogy and to those students of physics who are interested in the phenomena of polarized light.

J. S. A.

DIE ELEKTROLYSE GESCHMOLZENER SALZE. Dritter Teil, Elektromotorische Kräfte. Von RICHARD LORENZ, Dr. phil. o. Professor für elektrochemie und physikalische Chemie am eidg-Polytechnikum in Zurich (Monographien über angewandte Elektrochemie). Mit 75 in den Text gedruckten Abbildungen. Halle a. S.: Druck und verlag von Wilhelm Knapp. pp. 322. 1906. Price, M. 10.

The earlier parts of this monograph on the electrolysis of fused salts have already been noticed earlier.¹ The third part, as the title implies, deals with electromotive force. The subject is treated under the five general headings: Polarization, Elements, Electromotive Force and Chemical Heat (Free Energy), Decomposition Tension and the Ionic Theory.

This portion of the monograph seems to have been worked up with the same thoroughness as those that preceded it.

H. C. J.

GRUNDRISS EINER ENTWICKELUNGSGESCHICHTE DER CHEMISCHEN ATOMISTIK, zugleich Einführung in das Studium der Geschichte der Chemie. By DR. RICHARD EHRENFELD, Privatdozenten an der k. k. technischen Hochschule in Brünn. Heidelberg: Carl Winter's Universitätsbuchhandlung. 1906. pp. viii + 314.

The author has sought to bring together, in systematic form and historical sequence, the various steps in the development of the conceptions of the constitution of matter which led to the formulation of Dalton's atomic hypothesis. He has included the purely speculative notions as well as the hypotheses which have been the outcome of experimentation and begins with such early Greek conceptions of the constitution of matter as those of Anaxagoras, Empedocles, Democritus and Epicurus. This is followed by a discussion of the period dominated by the Aristotelian philosophy and the relation of this period to that of alchemy, in which it is shown that the notions of the transformation of the simple elements, earth, air, fire and water, the one into the other, suggested the possibility of the transmutation of the metals. Alchemy, with its first faint suggestions of chemical science, is discussed at length, and also the spread of alchemy from Arabia into Christian lands. The teachings of Paracelsus, Van Helmont and others of their contemporaries lead up to the corpuscular theory of Robert Boyle, and this, in time, to the phlogistic

¹ THIS JOURNAL, 35, 373, 547 (1906).

theory and the first conceptions of a chemical compound. All of this is considered in its bearings upon the theory of Dalton, which is fully discussed, from the point of view of its limitations, as well as its usefulness. The author then considers, at length, some of the views more recently expressed regarding the probable complexity of the atoms as conceived by Dalton, especially those of Thomson and of Rutherford and Soddy, based upon the study of the radio-active elements. In conclusion, he presents, in outline, the position of Wald and that of Ostwald, who deduce the fundamental principles, such as the laws of constant and multiple proportions, without recourse to any conception of the existence of a chemical atom, such as the hypotheses of Dalton presupposes.

The book should be of interest to students of the history of chemistry, as the author takes pains to point out the influence exerted by each school of philosophers and thinkers upon those succeeding them, and to demonstrate the dependence of the teaching of each school upon some of the earliest of the philosophers. The work is of a specialized character, as indicated by the outline above, and would not serve as a general text-book of the history of the science.

H. P. TALBOT.

AMERICAN CHEMICAL JOURNAL

THE REACTION BETWEEN UNSATURATED COM- POUNDS AND ORGANIC MAGNESIUM COM- POUNDS.

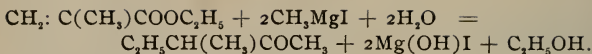
X. REACTIONS WITH α -METHYLCINNAMIC ACID.

BY E. P. KOHLER.

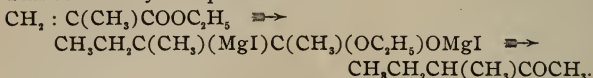
The principal object in investigating the reaction with methylcinnamic acid was to determine the influence of a "positive" group in the α -position of unsaturated esters. In an account¹ of the results obtained with benzalpropiophenone it was shown that the reactions with this substance, which has α -methyl, are exactly like those with benzalacetophenone. Since the publication of that account, Blaise and Courtot² have studied the reaction between Grignard's reagent and methacrylic acid and obtained results that they attribute to direct union of the reagent to the double linkage between carbon atoms. With methylmagnesium iodide, for example, they got, in addition to the tertiary alcohol expected, variable quantities of a saturated ketone, formed according to the equation :

¹ THIS JOURNAL, 31, 655.

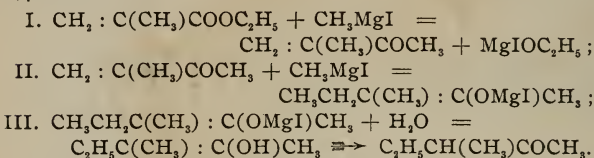
² Compt. rend., 140, 370.



This result they interpret as follows :



The authors offer no evidence in support of this interpretation and it seemed much more likely that the result was due to 1,4-addition, *viz.* :

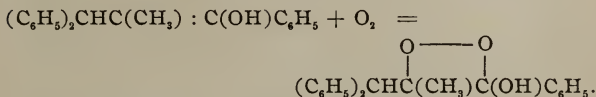


This view is established by the results described in the present paper.

The first reaction between methyl α -methylcinnamate and an organic magnesium derivative invariably consists in the replacement of methoxyl by a hydrocarbon residue, the product being an unsaturated ketone. As was shown in an earlier paper, this replacement reaction is greatly influenced by the nature of the group in the α -position. The effect of α -methyl is shown by the following table :

Ester.	Magnesium compound.	Per cent of product formed by replacement of OR.	Per cent of product formed by 1,4-addition.
$\text{C}_6\text{H}_5\text{CH} : \text{C}(\text{CH}_3)\text{COOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	96	4
"	CH_3MgI	100	0
$\text{C}_6\text{H}_5\text{CH} : \text{CHCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	50	50
"	CH_3MgI	100	0
$\text{C}_6\text{H}_5\text{CH} : \text{CBrCOOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	30	70
"	CH_3MgI	100	0
$\text{C}_6\text{H}_5\text{CH} : \text{C}(\text{C}_6\text{H}_5)\text{COOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	0	100
"	CH_3MgI	100	trace
$\text{C}_6\text{H}_5\text{CH} : \text{C}(\text{CN})\text{COOR}$	$\text{C}_6\text{H}_5\text{MgBr}$	0	100
"	CH_3MgI	0	100

In case an excess of reagent is present the unsaturated ketone immediately reacts with a second molecule and forms either the magnesium derivative of a tertiary alcohol by addition to carbonyl, or the derivative of an unsaturated alcohol by 1,4-addition, as represented by equation II. The most convincing proof of 1,4-addition was obtained when the magnesium derivative was carefully decomposed with iced acid. The resulting ethereal solution, when heated, gave only unsaturated ketone; but when it was evaporated at low temperatures, in a current of moist air or oxygen, the result was a peroxide. This behavior, as was shown in my last paper, is typical of the unsaturated alcohols obtained by 1,4-addition to ketones:



In this connection a number of experiments were performed for the purpose of determining to what extent this peroxide formation can be relied upon to prove 1,4-addition. All the solutions that were tried were obtained by decomposing magnesium compounds that were known to be 1,4-addition products of unsaturated esters or ketones. The results are shown in the following table:

Substance.	Amount of peroxide.
$(\text{C}_6\text{H}_5)_2\text{CHCH} : \text{C}(\text{OH})\text{C}_6\text{H}_5$	none
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH} : \text{C}(\text{OH})\text{C}_6\text{H}_5$	"
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{CH}_3) : \text{C}(\text{OH})\text{C}_6\text{H}_5$	95 per cent
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3) : \text{C}(\text{OH})\text{C}_6\text{H}_5$	92 "
$(\text{C}_6\text{H}_5)_2\text{CHCBr} : \text{C}(\text{OH})\text{C}_6\text{H}_5$	none
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5) : \text{C}(\text{OH})\text{C}_6\text{H}_5$	96 per cent
$\text{C}_6\text{H}_5\text{CH}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5) : \text{C}(\text{OH})\text{C}_6\text{H}_5$	"
$(\text{C}_6\text{H}_5)_2\text{CHCH} : \text{C}(\text{OH})\text{OC}_2\text{H}_5$	none
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_6\text{H}_5) : \text{C}(\text{OH})\text{OCH}_3$	"
$\text{C}_6\text{H}_5\text{CH}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5) : \text{C}(\text{OH})\text{OCH}_3$	"
$(\text{C}_6\text{H}_5)_2\text{CHC}(\text{C}_2\text{H}_5) : \text{C} : \text{NH}$	"

As will be seen, peroxides were obtained from enols derived from ketones with a hydrocarbon residue in the α -position and only from these. In all other cases the rearrangement from

the enolic to the corresponding saturated compound took place so rapidly that the latter began to separate from solution even before all of the magnesium derivative had been decomposed. These results may, at first sight, appear to be at variance with a very general conclusion reached by a careful study of tautomerism, namely, that alkyl derivatives are less extensively enolized than the substances from which they are derived. That conclusion, however, refers only to a final condition, while these results depend upon the rate at which an enol, that is obtained by indirect methods, passes into the only stable form.

EXPERIMENTAL PART.

The methylcinnamic acid used in the following experiments was made by Perkin's reaction, using benzaldehyde, propionic anhydride and sodium propionate. By neutralizing the product with an excess of sodium carbonate and crystallizing the salts from a solution of the carbonate it was possible to separate 2 sodium salts, corresponding to the 2 acids described by Raikow¹ and by Dain.² From a solution of the less soluble salt that separates from the sodium carbonate solution in solid form, acids precipitated pure, high-melting acid. This crystallized from ligroin in needles, melting at 81°. The more soluble salt that accumulated in the filtrates gave, mainly, the low-melting acid, which separated from ligroin in plates and melted at 74°. In this way it was comparatively easy to get the isomeric acids in any desired quantity, but all efforts to get the corresponding methyl esters failed. All methods of procedure gave the same ester from both acids.

Reactions with Phenylmagnesium Bromide.

In a preliminary experiment the reagent was very slowly siphoned into a dilute ethereal solution that contained a little more than one equivalent of ester and was cooled in a freezing mixture. The oil obtained by treating the resulting magnesium derivative in the usual way, was fractioned under diminished pressure and thus separated into unchanged ester

¹ Ber. d. chem. Ges., 20, 3397.

² Centrabl., 1898, I., p. 674.

melting at 39° , a pale yellow oil boiling at 212° (25 mm.) and a small quantity of solid melting at 102° . The oil forming the principal product of the reaction was identified as benzalpropiophenone. It reduced a solution of potassium permanganate in acetone and gave a phenylhydrazone melting at 131° . The solid melting at 102° was diphenylpropiophenone, previously described¹ as the sole product of the reaction between benzalpropiophenone and phenylmagnesium bromide. This experiment shows that the first reaction between methyl methylcinnamate and phenylmagnesium bromide consists in the replacement of methoxyl by phenyl.

When the reaction is carried out in the ordinary manner—the ester being added to a cooled, ethereal solution of the magnesium compound—the unsaturated ketone first formed immediately combines with a second molecule of phenylmagnesium bromide and the sole product is diphenylbutyrophenone. By operating in boiling ethereal solution it is possible to get a small quantity of saturated ester (ca 3 per cent) formed by direct addition to the ester. This fact was established by boiling the entire product with alcoholic potassium hydroxide and extracting the salt with water. From the aqueous solution hydrochloric acid precipitated a solid which was identified by comparison with a specimen of diphenylisobutyric acid on hand.

Triphenylmethylpropenyl Benzoate,

$(C_6H_5)_3CHC(CH_3) : C(C_6H_5)OCOC_6H_5$.—To prove that diphenylbutyrophenone is formed by 1,4-addition, the intermediate magnesium derivative was treated with slightly more than 1 equivalent of benzoyl chloride. The product, purified by recrystallization from a mixture of chloroform and alcohol, melted at 122° . Analysis :

0.1155 gram substance gave 0.3670 gram CO_2 and 0.0623 gram H_2O .

	Calculated for $C_{29}H_{24}O_2$.	Found.
C	86.1	86.5
H	5.9	5.9

¹ THIS JOURNAL, 31, 655.

The substance crystallizes in needles. It is readily soluble in acetone and chloroform, moderately in boiling alcohol and ether, very slightly in ligroin. Cold alcoholic potassium hydroxide rapidly hydrolyzes it to benzoic acid and diphenylbutyrophenone.

Diphenylbrombutyrophenone, $(C_6H_5)_2CHCBr(CH_3)COC_6H_5$.—The magnesium derivative of triphenylmethylpropenol readily reacts with 1 atom of bromine. The product separates from a mixture of ether and ligroin in large, lustrous tables, melting at 93° . The same substance is obtained when a chloroform solution, containing calculated quantities of diphenylbutyrophenone and bromine, is warmed on a water-bath, but the yield obtained by this method is much poorer and it is difficult to get rid of secondary products. Analysis:

0.1372 gram substance gave 0.3500 gram CO_2 and 0.0630 gram H_2O .

	Calculated for $C_{22}H_{19}OBr$.	Found.
C	69.65	69.50
H	5.01	5.12

The bromide is readily soluble in chloroform, moderately in alcohol and ether, sparingly in ligroin. It has not, as yet, been possible to eliminate hydrobromic acid and get an unsaturated ketone. Concentrated, alcoholic potassium hydroxide, which readily removes hydrobromic acid from analogous substances that have hydrogen¹ or phenyl² in place of methyl, in this case produces deep-seated decomposition, resulting in a number of products of which benzoic acid and diphenylmethane have been isolated and identified.

Triphenylmethylpropenol Peroxide,

$$\begin{array}{c} O \text{ --- } O \\ | \qquad | \\ (C_6H_5)_2CHC(CH_3)C(OH)C_6H_5 \end{array}$$

—When the magnesium derivative obtained by treating either benzalpropiophenone or methyl methylcinnamate is very carefully decomposed with iced hydrochloric acid, and the resulting ethereal solution

¹ THIS JOURNAL, 33, 41.

² *Ibid.*, 36, 195.

rapidly evaporated in a current of air or oxygen, as directed in a previous paper, about 96 per cent of the product is obtained in the form of a peroxide. In solution this is much less stable than the peroxides previously described, hence it is difficult to get a perfectly pure substance. The crude product was first dried thoroughly over phosphorus pentoxide in a vacuum desiccator, then repeatedly extracted with small quantities of low-boiling ligroin and finally recrystallized from a mixture of absolute ether and low-boiling ligroin. It separated in colorless needles, melting at 127° , and was readily soluble in all common organic solvents except ligroin. Analysis:

I. 0.1883 gram substance gave 0.5470 gram CO_2 and 0.1020 gram H_2O .

II. 0.1554 gram substance gave 0.4535 gram CO_2 and 0.0828 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_3$.	I.	Found. II.
C	79.5	79.22	6.02
H	6.0	79.52	5.94

The Molecular Weight in Boiling Ether.

$$K = 21.6.$$

Solvent. Grams.	Substance. Grams.	Rise in boiling point.	Molecular weight.
45.42	0.8360	0.127	313
"	1.4150	0.209	322
"	2.0540	0.302	323
Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_3$,			332

When perfectly pure the peroxide seems to be stable at the ordinary temperature. A specimen that has been kept in an open vessel for a year has changed neither in color nor melting point. Impure specimens rapidly turn yellow and occasionally explode. On a steam-bath the pure substance gradually softens, then explodes with a flash but without detonation. The same explosion takes place the instant the substance is melted. The products of decomposition by heat are quite different from those obtained from the peroxide that differs from this only in having phenyl in place of methyl.

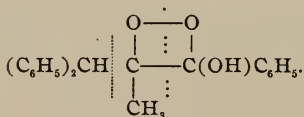
By exploding 25 grams in small portions and treating the resulting products as described in the last paper,¹ it was possible to isolate 7.2 grams of benzoic acid, 9.1 grams of a solid melting at 208°–210°, and a small quantity of diphenylmethane. The solid was purified by recrystallization from chloroform, from which it separated in flat needles. Analysis:

0.1540 gram substance gave 0.5280 gram CO₂ and 0.0910 gram H₂O.

	Calculated for C ₂₆ H ₂₂ .	Found.
C	93.4	93.5
H	6.6	6.5

Composition and melting point indicated symmetrical tetraphenylethane. It was identified as such by comparison with a specimen made from diphenylbrommethane.

The remaining products of decomposition were not identified, but it is evident that the peroxide molecule breaks down at two points:



Decomposition at these points should give 8.4 grams of benzoic acid and 12.5 grams of tetraphenylethane.

A similar decomposition into benzoic acid and tetraphenylethane took place when the peroxide was warmed with concentrated alcoholic potassium hydroxide; but by adding it slowly to a dilute solution, that was kept cool with ice-water, it was possible to isolate an intermediate product. This separated slowly from the alkaline solution in colorless plates. It was purified by recrystallization from a mixture of acetone and alcohol. It is readily soluble in chloroform, moderately in acetone, very slightly in alcohol and ether. The melting point is 188°. Analysis:

¹ THIS JOURNAL, 36, 189.

I. 0.1378 gram substance gave 0.4205 gram CO_2 and 0.0713 gram H_2O .

II. 0.1700 gram substance gave 0.5210 gram CO_2 and 0.0963 gram H_2O .

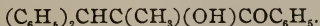
	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$.	I.	Found.	II.
C	83.6	83.22		83.7
H	6.3	6.5		6.3

Molecular Weight in Boiling Ether.

$$K = 26.1.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
20.10	0.4890	0.213	298
"	0.7830	0.361	282
"	0.9810	0.436	293
	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$,		316

The substance is evidently a reduction product formed from the peroxide by loss of one atom of oxygen. On distillation it decomposes into tetraphenylethane, benzoic acid and volatile hydrocarbons. Reagents like potassium hydroxide, hydroxylamine, acetic anhydride and glacial acetic acid produce essentially the same decomposition, but the principal product is diphenylmethane, in place of tetraphenylethane. The first definite clue as to the structure was supplied by the behavior towards methylmagnesium iodide. When a solution of this reagent was siphoned into an excess of the substance methane was evolved, until the solution contained approximately 1 molecule of the reagent for 1 of the substance. This proved the presence of one, and only one, hydroxyl group, and suggested as the most probable formula :



This structure was definitely established by the following method of preparation :

α -Bromdiphenylbutyrophenone, as stated above, is completely decomposed by concentrated, alcoholic potassium hydroxide, but by cautiously adding dilute, aqueous hydroxide, in small quantities, to a cooled solution of the bromide, it is

possible to replace the bromine quantitatively with hydroxyl. The product of this reaction is identical with that obtained from the peroxide. That substance is, therefore, α -hydroxydiphenylbutyrophenone. The only other substance of this composition that could be obtained from the bromide would be the corresponding β -hydroxy derivative, which might be formed by elimination of hydrobromic acid and subsequent addition of water. The substance cannot be a β -hydroxy compound, however, because it gives tetraphenylethane on distillation and diphenylmethane with potassium hydroxide.

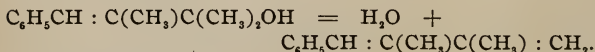
Reaction with Methylmagnesium Iodide.

Methyl methylcinnamate reacts with 2 molecules of methylmagnesium iodide, even though the magnesium compound be slowly siphoned into an excess of ester. The first reaction doubtless results in the formation of an unsaturated ketone, but this combines with more reagent so readily that it is impossible to separate the replacement and addition reactions. As is the case with benzalacetone and other methyl ketones, so here the addition is wholly to the carbonyl group. The product is an oil that, when heated under diminished pressure, begins to lose water at 150° and passes into a hydrocarbon that boils at 165° (30 mm.). Analysis :

0.2073 gram substance gave 0.6917 gram CO_2 and 0.1645 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{14}$.	Found.
C	91.1	91.0
H	8.9	9.2

The substance is phenyldimethylbutadiene, formed according to the equation :



Contributions from the Chemical Laboratory of Harvard College.

ON ETHYL PYROMUCYLACETATE.

[PRELIMINARY PAPER.]

BY HENRY A. TORREY AND J. E. ZANETTI.

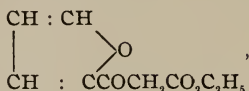
This compound was first prepared by Sandelin¹ in 1900, by the action of sodium on a mixture of 2 molecules of ethyl acetate and 1 of ethyl pyromucate. The aim of his research was, however, the preparation of methylfurfuryl ketone, which he obtained by saponifying the ester with concentrated sulphuric acid, the ester itself being but little investigated. Subsequently, Bouveault,² in his research on acetyl furfurane, repeated Sandelin's work on the ester but proceeded no further. Since the work which has been done upon this substance is so inconsiderable, we have undertaken its investigation in continuation of the work in this laboratory of the late Professor H. B. Hill on the furfurane derivatives.

The ester itself was obtained by Sandelin's method as a light yellow, heavy oil, boiling at 143°-145° (10 mm.). By using small amounts at a time, 15 grams of ethyl pyromucate and 20 grams of ethyl acetate, the best yields of 40-50 per cent were obtained. The use of potassium instead of sodium had no perceptible advantage. Both the ethyl acetate and the ethyl pyromucate were purified and freed from water before using, the ethyl acetate by drying over calcium chloride and distilling and the ethyl pyromucate by distilling under reduced pressure. This was found to be necessary, as some pyromucic acid is always carried down by the ethyl pyromucate in its preparation and distils over with the pyromucylacetic ester if not removed beforehand. The product of the first distillation carries over with it a sharp smelling compound which, if allowed to remain with the ester, slowly turns it dark. If the ester is redistilled, however, and the first fraction rejected, it keeps its light color for weeks and has practically no smell. Only after long standing does it become brown.

¹ Ber. d. chem. Ges., **33**, 492.

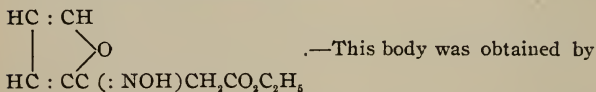
² Bull. Soc. Chim., [3], **25**, 435.

If ethyl pyromucylacetate is given the ketone formula, it would be represented thus :



but doubtless tautomeric relationships will be found here as with ethyl acetacetate and similar compounds. As would be expected, ethyl pyromucylacetate shows the characteristic ketone reactions, forming an oxime, a semicarbazone and, with phenylhydrazine, a pyrazolone.

Oxime of Ethyl Pyromucylacetate,



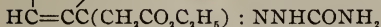
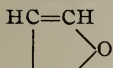
allowing 1 molecule of hydroxylamine hydrochloride, treated with a solution of sodium acetate, to act on 1 molecule of the ester, in a dilute alcohol solution. After letting the mixture stand for about 3 hours at room temperature and adding considerable water, the mass of long, white crystals was filtered by suction and recrystallized from dilute alcohol. After 3 crystallizations the constant melting point, $131^\circ\text{--}132^\circ$, was reached. Thus crystallized, the oxime consists of long, silky needles, soluble in a mixture of ether and alcohol. Analysis of the substance dried *in vacuo* over sulphuric acid :

I. 0.3995 gram substance gave 28.80 cc. of nitrogen at $20^\circ.6$ and 753 mm.

II. 0.1887 gram substance gave 12.68 cc. of nitrogen at $15^\circ.2$ and 760 mm.

III. 0.4008 gram substance gave 26.70 cc. nitrogen at 23° and 747 mm.

	Calculated for $\text{C}_9\text{H}_{11}\text{O}_4\text{N}$.	I.	Found. II.	III.
N	7.11	8.15	7.86	7.34

Semicarbazone of Ethyl Pyromucylacetate,

.—This compound

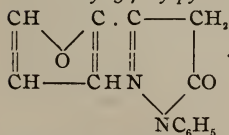
was formed by treating 1 molecule of the ester, in dilute alcohol solution, with 1 molecule of semicarbazide hydrochloride and the corresponding amount of sodium acetate. After standing for about 3 hours white crystals separated out. These were filtered off, washed with water and recrystallized from hot, absolute alcohol until a constant melting point was reached at 142° – 144° . The substance crystallizes in small, flat, rhombic plates which decompose slightly on melting. They are soluble in hot, absolute alcohol, hot benzene and hot chloroform, but insoluble in ligroin, hot or cold.

Analysis of substance dried over concentrated sulphuric acid *in vacuo* :

I. 0.1953 gram substance gave 30.95 cc. nitrogen at $25^\circ.7$ and 757 mm.

II. 0.2502 gram substance gave 41.38 cc. nitrogen at $22^\circ.5$ and 747 mm.

	Calculated for $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_3$.	I.	Found. II.
N	17.57	17.55	18.37

1-Phenyl-3-furylpyrazolone,

.—This compound was prepared by

Sandelin, by the action of 1 molecule of phenylhydrazine on 1 molecule of the ester, at 100° . After about 0.5 hour the mass solidifies and, by washing with alcohol and crystallizing from hot alcohol, the body is obtained as a white, crystalline mass of minute leaflets, melting at 179° . This substance has proved to be a very interesting one and we have prepared several of its derivatives. It is readily soluble in alkalis, pre-

precipitating from the solution on neutralizing with acid. If excess of acid be added, however, it redissolves. The pyrazolone itself, untreated with alkali, is soluble with difficulty only in concentrated acid. The above formula is that given by Sandelin. It is possible, however, that it may have a tautomeric form.

Acetyl Phenylfurylpyrazolone, $C_{13}H_9O_2N_2.COCH_3$. — This compound was readily obtained by dissolving the pyrazolone in boiling acetic anhydride and pouring the solution into water, when an oil separated which, on scratching, crystallized to a yellowish-white mass. The crystals were filtered off and recrystallized from ligroin several times to a constant melting-point. The melting point is not very sharp, lying between 69° – 72° . Under the microscope the crystals appeared as flat, transparent prisms, slightly yellow in color. They are soluble in alcohol, benzene and ether without difficulty, but insoluble in cold ligroin.

0.4196 gram substance gave 39.81 cc. nitrogen at 25° and 756 mm.

	Calculated for $C_{15}H_{12}O_2N_2$.	Found.
N	10.44	10.52

The *benzoyl derivative*, $C_{13}H_9O_2N_2.COC_6H_5$, was obtained by the Schotten-Baumann reaction. The pyrazolone was dissolved in sodium hydroxide and an excess of benzoyl chloride added. After some time a yellowish mass of crystals separated. These were filtered, washed and crystallized from dilute alcohol, whence they were obtained as white needles which, after 3 crystallizations, gave the constant melting point 113° – 114° . The body is soluble in alcohol and ether.

0.2084 gram substance, dried over concentrated sulphuric acid, gave 15.81 cc. nitrogen at 21° and 763 mm.

	Calculated for $C_{20}H_{14}O_2N_2$.	Found.
N	8.48	8.69

The *nitroso derivative*, $C_{13}H_9N_2O_2.NO$, was obtained by adding to an acid solution of the pyrazolone, in dilute alcohol, di-

lute sodium nitrite until starch-iodide paper indicated the presence of an excess of nitrous acid. The nitroso body separates out as a bright red precipitate as the sodium nitrite is added. It dissolves in dilute alcohol on warming, and, on cooling, separates out as an amorphous precipitate. No trace of crystallization could be detected under the microscope, even from solutions allowed to evaporate spontaneously. The body is soluble in alcohol, benzene, methyl alcohol, ether, chloroform and acetone, but insoluble in water. It gives no sharp melting point, but begins to soften at about 170° and gradually melts till at 183° – 184° it decomposes, giving off bubbles of gas and becoming dark brown. It is very hygroscopic, gaining as much as 4 milligrams in the course of a weighing if this be carried on without protection from the air. Dried over sulphuric acid *in vacuo* :

0.1961 gram substance gave 27.30 cc. nitrogen at 21° and 772 mm.

	Calculated for $C_{12}H_9O_3N_3$.	Found.
N	16.48	16.12

The study of these compounds will be continued in this laboratory.

METATOLYL ETHER AND DERIVATIVES.

BY ALFRED N. COOK.

Metatolyl ether, $(C_6H_4.CH_3)_2O$, was first obtained by J. H. Gladstone¹ and Alfred Tribe. They prepared aluminum thymolate, which they believed to decompose on heating, into aluminum metacresolate and propylene, the first compound then decomposing into metatolyl ether and other compounds. They made an analysis of the ether and determined its approximate boiling point, but did not investigate its properties further, hence a continuation of the study of the compound was deemed profitable.

Preparation.—All of the phenyl ethers so far obtained have been prepared by distilling the aluminum salts of the corre-

¹ J. Chem. Soc., 41, 11.

sponding phenols, but phenyl ether has also been prepared by several other methods. The preparation of aluminum metacresolate was found to be possible, although this seems to be the only "aluminum phenolate" not obtained by Gladstone and Tribe, perhaps because the action of aluminum on metacresol is brought about in a somewhat different manner from its action on other phenols. It is also possible that the aluminum they employed was much purer than the modern commercial article which was used in this research. From experiments already described¹ it would seem that the action of aluminum on phenols is electrolytic in character, and for the reason that a very pure aluminum would not contain sufficient impurities to set up local action it would be without action upon phenols, unless a catalytic agent like iodine should be employed.

The remarks made in connection with the preparation of aluminum phenolate² mostly apply to the preparation of this compound. Gladstone and Tribe found that a little iodine served to start the action of aluminum on several alcohols, phenol, ortho- and paracresol, etc., but the use of iodine or any other catalytic agent, unless aluminum metacresolate be so considered, was found to be of no avail in inducing the action of aluminum on metacresol.

The action was started by simply boiling metacresol with a few grams of aluminum strips, in a flask fitted with a reflux condenser, until the action began. The time required varied within wide limits, but was usually 3 or 4 hours; when once started, however, the action was very energetic and proceeded at a temperature much below the boiling point of metacresol. The action may be started very quickly and at a much lower temperature by simply adding a few grams of powdered aluminum metacresolate and a few strips of aluminum that have already been attacked by the cresol in a previous experiment and therefore have their impurities laid bare, thus supplying the conditions which exist when metacresol has acted on aluminum for a short time. In practice, the flask which had been used in a previous operation was employed, in which there

¹ J. Am. Chem. Soc., 28, 609.

² *Ibid.*, 28, 608.

always remained sufficient aluminum metacresolate adhering to the sides of the vessel to start up the action immediately, and very soon even with fresh aluminum slips.

Aluminum metacresolate is a brittle, translucent solid. It varies in color from gray to black and possesses a vitreous luster and a conchoidal fracture. In appearance it is very much like aluminum phenolate. It is usually a little moist with metacresol unless highly heated at the close of its preparation. When distilled *in vacuo* aluminum metacresolate yields a very little metacresol and a very large amount of a substance which boils at 240° (30 mm.) and decomposes when distilled under ordinary atmospheric pressure. It solidifies at room temperature, melts when gently heated and is an entirely different compound from the 2 higher boiling substances obtained by distilling under ordinary atmospheric pressure, which are mentioned below. The odor of the distillate would indicate that a small amount of metatolyl ether was formed, but not sufficient to separate by fractional distillation.

When distilled under ordinary atmospheric pressure, there was obtained a considerable amount of metacresol, a fair yield of metatolyl ether, a solid substance, boiling at about 300° (uncorr.), and a red liquid boiling at approximately 360° . The higher boiling substances were not examined but were set aside for further study when time permits.

From 850 grams of aluminum metacresolate there was obtained, after repeated fractional distillation, 110 grams of purified metatolyl ether and there resulted 150 grams of metacresol. The best yield of the ether was obtained by distilling rapidly. When distilled slowly there was obtained a much larger yield of metacresol and higher boiling substances. It may be noted that the reverse was found to be true in the preparation of phenyl ether from aluminum phenolate, a much larger yield of the ether being obtained when the phenolate was distilled slowly.

Purification.—Gladstone and Tribe extracted the metatolyl ether from the higher boiling substance, which they assumed, provisionally, to be dimethylbenzophenone, by means of

ether and cooling to -20° , at which temperature the substance is only slightly soluble. They seem not to have obtained the red liquid boiling at about 360° . I obtained an equally pure product by repeated simple fractional distillation. After the separation of the metacresol, which boils about 75° lower, had been carried as far as practicable, and discarding each time the fractions boiling above 290° , the liquid was washed with a solution of sodium hydroxide to remove traces of phenol, and dried with calcium chloride by gentle warming on the water-bath. On again distilling for perhaps a dozen times it had a fairly constant boiling point. A still purer product was obtained by distilling off the metatolyl ether with steam, after washing with sodium hydroxide, but the process is somewhat tedious.

Boiling Point.—The boiling point as given by Gladstone and Tribe is 284° – 288° , presumably uncorrected. The determination of the boiling point on 2 different samples, one prepared by extracting with ether and the other by fractional distillation, yielded identical results. The boiling point obtained was $290^{\circ}.5$ – $291^{\circ}.5$ (cor.). The thermometer was calibrated by means of naphthalene and benzophenone and required but a small correction.

Viscosity.—The viscosity was determined with an apparatus designed for use in testing lubricating oil and was not susceptible to a high degree of accuracy.

Table of Viscosity.

Temperature.	Viscosity.	Difference.
$15^{\circ}.5$	1.333	. .
30°	1.194	0.139
40°	1.166	0.028
50°	1.139	0.027

It will be noticed that there is a very marked decrease in viscosity between $15^{\circ}.5$ and 30° and above this temperature the decrease is practically constant for 20° . The most rapid decrease was found to be between $15^{\circ}.5$ and 25° . The viscosity of phenyl ether was found to be 1.095 at 30° . The vis-

cosity of metatolyl ether is, therefore, 9.4 per cent greater at the same temperature, notwithstanding its lower specific gravity.

Properties.—Metatolyl ether is an aromatic, oily substance. It has the odor of geraniums, but is considerably less marked in that respect than phenyl ether. The constant breathing of its vapors has a depressing effect upon the system. It is tasteless, but feels like an oil when taken into the mouth. The specific gravity, determined with a pyknometer, was found to be 1.0323 at 21°, average of 3 determinations which did not vary more than 3 parts in the ten-thousandths place. This is nearly 4 per cent less than liquid phenyl ether at the same temperature, notwithstanding its larger molecule. When prepared by distillation, as described above, it is slightly fluorescent and has a yellowish tint which increases with age, but when purified by distilling with steam it is devoid of fluorescence and is almost colorless. It burns readily with a smoky flame, liberating a large amount of soot. It is insoluble in water, but soluble in most of the common organic solvents and also in a strong solution of sodium metacresolate in water, from which it is precipitated on adding a large amount of water. It is volatile with steam, but considerably less so than phenyl ether.

Action of Reagents.—Attempts to prepare a sulphonic acid derivative with dilute and concentrated sulphuric acid, and fuming sulphuric acid, under varying conditions, were without avail. Phenyl ether yields a disulphonic acid with great ease by simply dissolving in an equal volume of sulphuric acid. Monosulphonic acid derivatives of *p*-nitro-*m*-methylphenyl ether and *o*-nitro-*m*-methylphenyl ether are also formed with great readiness and this failure would seem to indicate that the sulphonic acid group entered the nucleus with the nitro group in the nitromethylphenyl ethers.

Endeavors to oxidize the side chains to carboxyl, with chromic acid in acetic acid solution, were unsuccessful. An aqueous solution of chromic and acetic acid does not attack it when boiled. Chromic acid, in glacial acetic acid, oxidizes it to a fine, white powder which is precipitated on standing when

diluted with a large amount of water. The substance is insoluble in alkalies.

Metatolyl ether is not decomposed by long-continued boiling with a strong solution of sodium hydroxide, nor even when heated in a closed tube to 200° , for several hours. In this respect it is like phenetol, anisol and phenyl ether.

When heated with concentrated, or even fairly dilute nitric acid, it yielded a dinitro compound, but not readily. The tendency is to oxidize completely and many attempts were made before success was finally attained. The best results were obtained with fuming nitric acid. Phenyl ether also yields a dinitro derivative with fuming nitric acid.

When the calculated amount of bromine was added to the substance in solution in carbon bisulphide in the dark, or, *per se*, in direct sunlight, heated to the boiling point, or, at the temperature of the boiling water-bath, at room temperature, or cooled to -20° , there was always formed, with equal facility, a dibrom compound which was identical in every instance.

When double the amount of bromine was added, or even a very large excess, there was produced, with equal readiness, a tetrabrom compound under the same varying circumstances.

Some of the tetrabrom compound was always formed in preparing the dibrom derivative by employing the amount required by calculation and there always remained a small quantity of the ether unacted upon, but only in small amount, and they were readily separated by fractional distillation. Likewise a little of the dibrom compound was obtained by employing the calculated amount of bromine to form the tetrabrom derivative, but the action was more clear cut than is usual in similar cases. It proved impossible to induce the substance to absorb more than 4 atoms of bromine no matter how large an excess was added. No carrier was used in these experiments. Hoffmeister¹ found that phenyl ether, when dissolved in carbon bisulphide, absorbed 2 atoms of bromine to the molecule.

I believe, for the following reasons, that the bromine en-

¹ Ann. Chem. (Liebig), 159, 210.

tered the nucleus in these experiments. The bromine derivatives effectually resisted all attempts to prepare from them compounds analogous to benzyl alcohol and benzaldehyde by all of the common methods. The bromine is very firmly linked in these compounds and all attempts to introduce the hydroxyl group in its place were unsuccessful. This is in accordance with what would be expected if the halogen entered the nucleus. Neither of the two compounds, when purified, gave off vapors which attack the mucous membrane of the eyes, as in case of substances formed by the halogen entering the side chain, but when freshly prepared, and before purification, they did have this property, indicating the possible formation of a small quantity of the side chain compounds. Perhaps the halogen might be induced to enter the side chain by employing a still higher temperature, in direct sunlight, but the experiment was not tried on account of lack of both time and material.

Metatolyl ether is markedly different from toluene and its homologues in its action toward bromine, for in these the halogen enters the side chain in direct sunlight, or at the boiling point of toluene, and it enters the nucleus in the dark, when cold.

Dibrommetatolyl Ether, $(\text{CH}_3\text{C}_6\text{H}_3\text{Br})_2\text{O}$.—This compound was best prepared by adding very gradually, with constant shaking, a little more than the theoretical amount of bromine to the metatolyl ether, dissolved in several times its weight of carbon bisulphide. The yield was but little short of quantitative. It was purified by repeated distillation, discarding the highest and lowest boiling fractions each time. A portion was obtained which melted at 48° , but began to soften a few degrees lower. The substance boils at 340° – 350° (uncorr.) under ordinary atmospheric pressure, and at about 250° (15 mm.). The dibrom compound is a white, crystalline solid, which turns yellow with age. It tends to crystallize in warty aggregations on cooling from the molten state. It is soluble in carbon bisulphide, alcohol, ether and several other organic solvents; sparingly soluble in absolute methyl alcohol and insoluble in water.

The substance was boiled with water and then with a strong solution of potassium hydroxide, in the hope of introducing the hydroxyl group in place of the halogen, but without result. It was then heated in a closed tube, to 200° , for several hours, with a strong solution of sodium hydroxide, but there was no indication of any reaction. Analysis :

	Calculated for $C_{14}H_{12}OBr_2$.	Found.
Br	44.94	44.55

Tetrabrommetatolyl Ether, $(CH_3C_6H_2Br_2)_2O$.—This compound was found to be best prepared by adding an excess of the amount of bromine required by calculation directly to the metatolyl ether and heating on the water-bath to drive off the surplus. The yield was nearly quantitative. The substance was purified by repeated distillation under diminished pressure. It boils at 260° – 270° (35 mm.), but decomposes when distilled under ordinary atmospheric pressure.

It is a light yellow, sticky, viscous substance which crystallizes in warty aggregations on standing for some time. It becomes fluid on gently heating and is soluble in carbon bisulphide but insoluble in alcohol, ether and most other common organic solvents. The compound was boiled with water, a strong solution of potassium hydroxide, and with water and precipitated calcium carbonate, respectively, for several hours without any evidence of chemical action. It was then heated in closed tubes with each of these reagents for 3 or 4 hours, at 200° – 300° . The tube containing the potassium hydroxide showed some signs of chemical action, but it was by no means complete. The filtrate yielded a precipitate with silver nitrate and a small quantity of a substance, presumably a hydroxymetatolyl ether, was precipitated by neutralizing with an acid. Analysis :

	Calculated for $C_{14}H_{10}OBr_4$.	Found.
Br	62.26	61.85

Dinitrometatolyl Ether, $(CH_3C_6H_3NO_2)_2O$.—It was found best

to prepare this substance in nearly the same manner as Hoffmeister¹ prepared the dinitro derivative of phenyl ether. By means of a dropping funnel fuming nitric acid was gradually and cautiously added to the substance, kept cool by running water, until the metatolyl ether was entirely dissolved. The solution was then poured into water when the nitro derivative was precipitated as a red, viscous mass. By repeatedly rubbing it up with cold water containing sodium hydroxide it finally solidified. It was then purified by repeated crystallization from alcohol and boiling with bone-black. Dinitrometatolyl ether is a yellow, crystalline substance which melts at 112°–113°. It is insoluble in water, but soluble in alcohol, ether, benzene, etc.; 1.4 parts of the substance are soluble in 1000 parts of 87 per cent alcohol at 20°, but it is much more soluble at higher temperatures. Its composition is shown by the analysis of the amino hydrochloride.

Diaminometatolyl Ether Hydrochloride, $(\text{CH}_3\text{C}_6\text{H}_3\text{NH}_2\text{HCl})_2\text{O}$. —This compound was easily and quickly prepared by reducing the nitro compound, in alcoholic solution, with tin and hydrochloric acid by gentle warming on the water-bath and precipitating the tin with hydrogen sulphide. On account of its great solubility in water, it was found best to purify it by crystallizing from concentrated hydrochloric acid, in which it is much less soluble. The hydrochloride is quite stable even when moist. With alkalies it yields a free *base* which is insoluble in water, but soluble in alcohol and ether. It also is quite stable, but less so than the hydrochloride. The latter yielded 23.98 per cent of chlorine; calculated for $\text{C}_{14}\text{H}_{18}\text{ON}_2\text{Cl}$, is 23.59 per cent.

A similar study is now being made of paratolyl ether. It will also be extended to the ortho compound as soon as possible.

UNIVERSITY OF SOUTH DAKOTA,
VERMILLION, S. D.,
June 19, 1906.

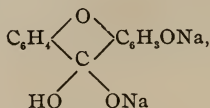
¹ Ann. Chem. (Liebig), 159, 208.

THE ISOMERISM OF ETHYLCOUMARIC AND ETHYL-COUMARINIC ACIDS.

BY ARTHUR MICHAEL AND ARTHUR B. LAMB.

In the course of his synthetical investigations of the substituted cinnamic acids, W. H. Perkin¹ made the interesting observation that methoxycinnamic acid, prepared from *o*-methoxybenzoic aldehyde and acetic anhydride, is not identical with the isomeric substance obtained by the action of methyl iodide on R. Williamson's² potassium coumarin product. These and the similar ethoxy derivatives were carefully investigated by Perkin and the results communicated in a later paper,³ together with a discussion of this peculiar case of isomerism. Perkin notes the resemblance between these and fumaric and maleic acids, as Baeyer had also done, and observes that, according to van 't Hoff's hypothesis, there should be two stereomeric coumaric acids. The chemical behavior of these acids led him, however, to believe that the cause of the isomerism in question is not connected with the unsaturated carbon atoms, simply concluding that "These facts would seem to indicate that in the α -compounds the groups, or some of them, contained in the molecules are *farther apart* than in the β -compounds."

In 1882 Roser⁴ suggested his now well-known structural explanation of the isomerism of maleic and fumaric acids and stated that the isomerism in the coumaric acid series might possibly be explained by analogous structures. In the following year one of us⁵ found that salicylresorcinolic ether unites with sodium hydroxide to form the compound,



¹ J. Chem. Soc., 31, 417.

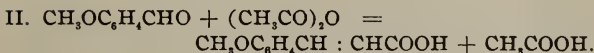
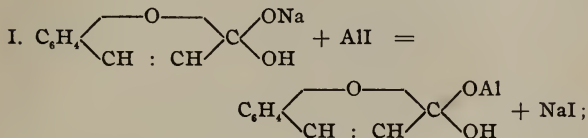
² *Ibid.*, 28, 850.

³ *Ibid.*, 39, 409.

⁴ Ber. d. chem. Ges., 15, 2348.

⁵ Michael: *THIS JOURNAL*, 5, 93.

and, assuming similar constitutions for Williamson's sodium derivative of coumarin,¹ he explained the isomerism of the alkylcoumarinic (I.) and alkylcoumaric acids (II.) in the following manner :



J. Wislicenus² revived the van't Hoff explanation for these and other cinnamic acid derivatives, but one of us³ shortly

¹ J. Chem. Soc., 28, 1850.

² Räuml. Anord. u. s. w., p. 53.

³ Michael: J. prakt. Chem., [2], 38, 15-27. The correct interpretation of the isomerism in the substituted unsaturated monobasic acids, and the first experimental proof that 2 isomers exist having the same structural constitution, as has been assumed by van't Hoff, was given by me in 1886. It was the impossibility of reconciling my results in the cinnamic acid series with the conclusions obtained by applying the van't Hoff hypotheses to these substances that mainly led me to my supposed conservative attitude. The further testing of the matter has clearly demonstrated how fruitless are all these immature stereomeric speculations. Indeed, the confused condition of the theory in organic chemistry is largely due to their pernicious influence. Wislicenus, in his endeavor to make experiment conform with his theoretical views, reversed the position of the halogen atoms in the monohalogen cinnamic acids, which I had previously proved experimentally. Two years later (Ann. Chem. (Liebig), 248, 354; cf. Michael: J. prakt. Chem., [2], 40, 42), although nothing new in the subject had been published except my criticism of his views, he discarded his own and accepted my classification. It is true, that in this paper he stated that the conditions of isomerism in the cinnamic series are the same as in the crotonic series, but in doing this he simply tardily acquiesced in the conclusions which I had drawn several years previously from my researches. After almost 20 years we are facing the stubborn fact that the conclusions which Wislicenus drew by a systematic application of the van't Hoff hypothesis are, without exception, absolutely untenable, and that our knowledge of the intramolecular atomic grouping consists largely of a collection of unproved and, among themselves, mainly contradictory assumptions. We do know now, however (*vide* Ber. d. chem. Ges., 34, 3646; 39, 203), that the van't Hoff hypothesis no longer gives the correct number of isomers, and that it cannot be safely used in any reaction which involves a simultaneous chemical change on 2 carbon atoms in the molecules.

afterwards showed that the configurations given by Wislicenus to these substances led to a maze of astonishing contradictions.

This case of isomerism is particularly noticeable, in that neither of the above explanations may be said to offer a comprehensive solution of all the facts we know about these acids. We shall here discuss some of the more marked divergencies between the theoretical conceptions and the actual chemical behavior of these substances.

Compounds of the fumaric acid type, when heated, if they can pass over by loss of water into dehydrated ring products, show a tendency toward such a change, which change necessarily implies a conversion into the maleic form. Now the fumaroid coumaric acid is exceedingly stable toward heat, even when the temperature is raised to a point where decomposition sets in. It simply undergoes a retrogressive change without the formation of any coumarin. On the other hand, Fittig and Ebert¹ have shown that it is only necessary to allow coumaric acid to stand at the ordinary temperature with saturated hydrobromic acid to convert it completely into coumarin; that is, a reagent that ordinarily transforms a maleic into a fumaric modification in this case induces the reverse change. It is possible, however, that this absence of harmony between chemical cause and stereomeric effect may be more apparent than real, for one of us² has shown that the usual relation between physical and chemical properties is actually reversed in the case of cinnamic acid. For instance, ordinary cinnamic acid, which is wholly fumaroid in its physical properties, gives, primarily, addition products which are not fumaroid but malenoid in character. If, then, the closely allied cinnamic acid undergoes a chemical change by the addition of hydrobromic acid, the primary tendency may be in the direction of forming a malenoid substance.

Morgan and Micklethwait³ have isolated a coumarin platinum chloride, $4\text{C}_9\text{H}_6\text{O}_2 \cdot \text{H}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$. This indicates that coumarin and hydrobromic acid unite to form a "molecular compound"

¹ Ann. Chem. (Liebig), **226**, 352.

² Michael: Ber. d. chem. Ges., **34**, 3644.

³ J. Chem. Soc., **89**, 863.

and not to form a brommellilotic acid. If the latter reaction took place, the lactone formation might be explained according to Wislicenus, *i. e.*, by rotation of the saturated configuration and elimination, first of water, then of hydrobromic acid. This principle, however, as a basis for stereomeric transformations has been given up, and to-day scarcely merits serious consideration. That it cannot be used in the present case follows from the experiments of Fittig and Hochstetter, who have shown that the stable saturated mellilotic acid is converted into its lactone at ordinary temperatures by hydrobromic acid.

Hjelt¹ has shown that coumaric acid does not exist in the free state even in the presence of water, going over into coumarin with surprising facility. On the other hand, Fittig and Hochstetter² found that the corresponding saturated compound undergoes the lactone condensation with great difficulty. This difference has been explained stereomerically,³ inasmuch as in coumaric acid the position of the hydroxyl and carboxyl groups are fixed by the unsaturated carbon atoms, while in the saturated configurations these groups are in a condition of gyration and hence a position favorable to the conversion occurs in certain periods of the revolution. This is one of the many stereomeric explanations which are widely accepted, but which will not bear a critical examination. If the ease of the lactone formation were solely dependent on such a condition, at the moment when the interested groups were in a proper juxtaposition the condensation process should go on with readiness. Since such a gyratory motion must be assumed to be extremely rapid, it follows that the difference between the extents of lactone formation of coumaric and mellilotic acids can be only one of degree. This explanation, therefore, fails utterly in explaining the non-existence of coumaric acid and the stability of its reduction product.

One of us⁴ has shown that the stereomeric explanation put forward by J. Wislicenus,⁵ for the formation of lactones, is un-

¹ Ber. d. chem. Ges., **27**, 3331.

² Ann. Chem. (Liebig), **226**, 357.

³ Harries, Meyer u. Jacobson, Lehrb. II., p. 674.

⁴ Michael: J. prakt. Chem., **60**, 338.

⁵ Räuml. Anord, etc., p. 68.

tenable and has pointed out that the process is really an intramolecular esterization, proceeding the more easily the less resistance there is in the molecule to the formation of the ring, and the recent investigations of Petrenko-Kritschenko and Konschin strongly confirm his view.¹ It is evident, therefore, that any change in the system which would facilitate esterization would bring about a more facile lactonization. Now mineral acids show such a catalytic effect to a marked degree and, consequently, it is not surprising that hydrobromic acid should favor the lactone formation in the above instances. Moreover, any chemical change in the structure of the side chain in mellilotic acid which accelerates the interaction between the hydroxyl and carboxyl groups must necessarily tend towards inducing easier lactonization. Such a change occurs with the unsaturation of the carbon atoms. This involves a greater accumulation of free energy on the carboxyl group, the fulcrum in the esterization process.

There is, indeed, an investigation in the fatty series which seems to point to the existence of stereomeric hydroxy acids resembling coumaric and coumarinic acids. Zelinsky,² by treating the addition product of hydrocyanic acid and acetylacetone with hydrochloric acid, obtained a monolactone of dimethyldihydroxyglutaric acid, which, on distillation, passed over into the dilactone. The lactonic acid, when heated with barium hydroxide, assimilates water and gives the salt of a dihydroxy acid, which, in the free state, spontaneously dehydrates into the original lactonic acid, while the dilactone, by a similar treatment, gave a stable dihydroxy acid. Zelinsky assumes that the stable form is the racemic modification, while the unstable form is optically active. It is, however, difficult to understand how any material change in the intramolecular gyration can be caused by racemization. This instance obviously offers no support to the Harries stereomeric explanation in the aromatic acids. It is to be regretted that this interesting subject has not been further investigated, as the assumptions of Zelinsky in regard to the constitution of

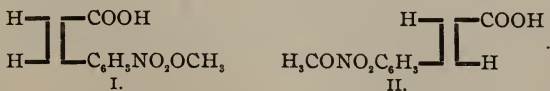
¹ Ann. Chem. (Liebig), **342**, 53.

² Ber. d. chem. Ges., **24**, 4006.

these products cannot be considered to be definitely established.¹ *Vide* also Rupe and Ronus.²

An interesting contribution to this subject was made by v. Miller and Kinkelin,³ in a research on the mononitro substitution products of the coumaric acid derivatives. They found that *o*-nitrocoumaric acid, in contrast with coumaric acid itself, is capable of free existence. This fact is, however, explicable from either of the above points of view. The increased stability of the $C(OH)_2$ group, when the carbon atom is subjected to strong negative influences, is a characteristic property of the grouping; on the other hand, the more negative character a carbinol assumes, the less easily it unites with an acid to form an ester. In the further observation, however, that dimethyl *o*-nitrocoumarinate, on being warmed with sodium carbonate and alcohol, is completely saponified, *i. e.*, goes over into *o*-nitrocoumarinic acid, while dimethyl *o*-nitrocoumarate, under similar treatment, yields *o*-nitromethoxycinnamic acid, which even continued boiling with alcoholic alkali but slowly converts into the hydroxy acid, is undoubtedly found to be a very serious argument against the stereomeric explanation. That the introduction of a nitro group into the ortho position in anisol derivatives renders the methoxy group somewhat more susceptible to saponification is easily understood from a theoretical point of view and has, indeed, been shown to be the case in several instances, but this grouping occurs in both the acids, and the marked contrast in their behavior towards alkalis cannot, therefore, be due to the influence of the nitro group alone.

Harries³ has endeavored to bring the stereomeric explanation into accord with these facts. The configuration of *o*-nitromethoxycinnamic acid (I.) and its isomer (II.) are:



¹ Ber. d. chem. Ges., 22, 1705.

² *Ibid.*, 34, 2191.

³ Meyer u. Jacobson, Lehrb., II., p. 674.

Harries directs attention to the fact that in I. the methoxy group is not only subjected to the action of the nitro group, but, much more than in II., to the negative influence of the carboxyl group. Harries, therefore, concludes that the relative ease of saponification of coumarinic acid is due to this difference and that the property agrees with the configuration of the compound. This is an argument which J. Wislicenus¹ frequently used in his speculations and which one of us,² years ago, showed to be based on fallacious reasoning. It is obvious that the first product formed when an acid and a base come in chemical contact must be a salt; therefore, it is no longer a question of the negative influence of the carboxyl group, but rather of the neutralized sodium derivative. Indeed, if we are to go back to known analogous instances, it may be safely stated that proximity of COONa should *increase* the resistance of the methoxy group to such a chemical change. In speculations on spacial influence it has been generally overlooked that such an influence is necessarily of a mutual character between the atoms or groups concerned. This is very noticeable in the present case; indeed, this point of view affords an explanation of some hitherto unexplained properties of phenolic derivatives. Thus, while salicylic acid, in aqueous solution, has a greater avidity than either the meta or para isomer,³ it acts towards aniline blue as a monobasic acid, while the para isomer exhibits the behavior of a dibasic acid.⁴ Again, the heat of neutralization of the 3 hydroxybenzoic acids, when treated with sodium hydroxide in molecular proportions, is practically identical. The addition of a second molecule of alkali gives a further evolution of 9.2 cal. with the 2 isomers of salicylic acid, but only 1 cal. with salicylic acid itself, so that it is doubtful if the disodium derivative can exist in the presence of water.⁵ This relationship is also shown with other reagents. Thus, dry salicylic acid absorbs only 1 molecule of ammonia, while the meta and para acids unite with double

¹ Ann. Chem. (Liebig), 248, 347.

² Michael: J. prakt. Chem., 40, 37.

³ Ostwald: *Ibid.*, [2], 32, 345.

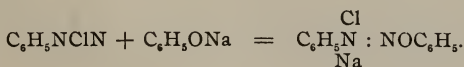
⁴ Engel: Ann. Chim. Phys., [6], 8, 573.

⁵ Berthelot and Werner: *Ibid.*, [6], 7, 146.

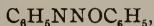
that amount. It also extends to the esters of the acids, as has been shown recently in this laboratory, while studying their behavior towards bases and other reagents. The explanation of these facts is obvious. Benzoic acid is a weak acid and, therefore, incapable of using up the positive energy of so strong a metal as sodium. For this reason, the more intimate the relationship of the second negative group, the hydroxyl, to the metal, the more complete must be the conversion of the residual negative energy in the molecule into bound energy or heat.

While the stereomeric explanation of Harries for the behavior of the nitro esters towards alkalis is untenable, it cannot be denied that the structural explanation of the isomerism is, in this respect, in good agreement with the facts.¹

Recently Borsche² has endeavored to settle this question experimentally in a new manner. He starts from the point of view that according to the structural explanation coumarinic acid is a phenyl ester, while stereometrically considered it is a phenol. Now, as diazobenzene chloride is without action on the first group of substances, but yields azo derivatives with the latter, Borsche believes that this reagent may be used to decide the question. He found that potassium coumarinate and diazobenzene chloride give benzeneazocoumarin and, therefore, concludes that the stereomeric configuration has been proved in a conclusive manner. This conclusion is, however, based on very imperfect reasoning. The primary action of sodium phenolate on diazobenzene chloride is of an additive nature.³



This product immediately decomposes into salt and



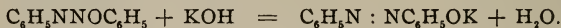
but, as the reaction takes place in the presence of an alkali and

¹ v. Miller and Kinkelin : Ber. d. chem. Ges., **22**, 1714.

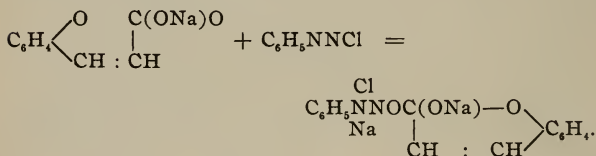
² *Ibid.*, **37**, 346.

³ Michael : *Ibid.*, **37**, 2098.

the new organic product has, within itself, the elements of instability, *i. e.*, an accumulation of negative atoms plus the possibility of an easy rearrangement to form a compound of a much more acidic nature than phenol, an intramolecular rearrangement does take place :¹



It is evident that a neutral phenyl ester could not form an addition product with diazobenzene chloride, but, and it is at this point that Borsche makes a mistake in his argument, there is no reason why such a basic compound as sodium coumarinate should not do so :



There exist, furthermore, the same conditions for the decomposition and rearrangement of the addition product into an azo derivative as when a phenolate is used.

It cannot be said, therefore, that the question whether coumaric and coumarinic acids are spacial or structural isomers has been conclusively settled, but there can be no doubt that spacial modifications of the hydroxycinnamic acids are capable of existence. Consequently, if the method used in preparing allocinnamic acid from cinnamic acid were employed with ethyl coumaric acid, the identity or non-identity of the product with ethylcoumarinic acid would be an argument in favor of one or the other view.

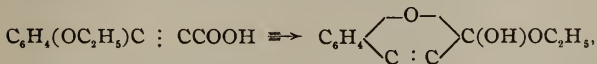
Cinnamic acid has been changed into allocinnamic acid by converting it into phenylpropionic acid, adding hydrobromic acid to this² and reducing the bromcinnamic acid, *m. p.* 159°.³ A similar series of manipulations with ethylcoumaric acid was

¹ Cf. Dieckmann : *Ber. d. chem. Ges.*, **37**, 3370, 4627. Michael : *Ibid.*, **38**, 22.

² Michael and Brown : *Ibid.*, **19**, 1378 ; **20**, 550.

³ Liebermann and Scholtz : *Ibid.*, **25**, 950.

found to yield an acid which proved identical with *ethylcoumarinic acid*. This is, indeed, a strong argument in favor of considering the relation between these acids as being similar to that existing between the stereomeric cinnamic acids. A rearrangement of the ethoxyphenylpropionic acid under the conditions of the experiment into a lactone derivative,



is excluded. Besides, if it did take place, the next step in the process would not have been the formation of a bromethoxycinnamic acid but bromcoumarin. Incidentally, the question was examined whether an acid corresponding to isocinnamic acid¹ is formed in the reduction of *o*-ethoxy- β -bromallocinnamic acid. We were, however, unable to discover any indication of its formation.

*Preparation of Ethylcoumarinic and Ethylcoumaric Acids.*²

These isomeric acids were first prepared by Perkin,³ who called them the α - and β -ethylcoumaric acids, respectively. Later, Ebert⁴ devised convenient methods for their preparation, which Claus,⁵ working afterwards in the same laboratory, also employed. But, strange to say, the β - or ethylcoumaric acid is best prepared by the method which Ebert gives for the preparation of the α -acid. According to his directions, coumarin (1 mol.) is dissolved in an *absolute* alcoholic solution of sodium alcoholate (2 mols.), and to this ethyl iodide (1 mol.) is added and the mixture digested for 3 hours. Ebert obtained, in this way, a good yield of ethylcoumarinic acid, m. p. 103°. We invariably obtained instead ethylcoumaric acid, m. p. 133°. Finally, influenced by the fact that Perkin employed an aqueous alcoholic solution of sodium hydroxide in his method of preparation, we substituted 96 per cent alcohol

¹ Erlenmeyer, sen : Ann. Chem. (Liebig), 287, 21. Michael : Ber. d. chem. Ges., 34, 3640; 36, 900. Erlenmeyer, jun : *Ibid.*, 37, 3361; 38, 837.

² This work was done in the winter of 1901.

³ J. Chem. Soc., 39, 412.

⁴ Ann. Chem. (Liebig), 216, 142 ff.

⁵ *Ibid.*, 269, 2.

for the absolute alcohol of Ebert's directions. A good yield of ethylcoumarinic acid was thereby obtained. Thus, 6 grams of coumarin, 1.9 grams of sodium, 6.6 grams of ethyl iodide and 50 cc. of 96 per cent alcohol were digested for 3 hours on the water-bath, the product was evaporated to dryness, water was added and the whole shaken with ether to remove the neutral oil. The aqueous solution was warmed, then cooled and acidified. The precipitate dissolved completely in cold sodium carbonate, showing that all of the coumarin had been converted into an acid. The melting point of the acid, without recrystallization, was 102° – 103° ; weight 4 grams. The ether extract was saponified with alcoholic potassium hydroxide and yielded 3.3 grams more of an acid melting at 95° – 97° . The total yield was 7.3 grams, the theoretical yield being 7.9 grams. It is, therefore, very probable that Ebert used an "absolute" alcohol which was not absolute. The ready conversion of coumarin into coumaric acid by sodium alcoholate is further evidenced by the impossibility of Ebert's method as given (cf. p. 579).

Obviously then, by simply employing either an absolute or a 96 per cent alcohol, one can prepare, in the first place, the high-melting ethylcoumaric, or, in the second case, the low-melting ethylcoumarinic acid, and each in excellent yield.

It was evident, in the above experiment, that small amounts of diethyl ester were formed, although coumarin and ethyl iodide were used in molecular proportions.

Preparation of Pure Ethyl Ethylcoumarate.

The ester, similarly to the acid, may be obtained directly from coumarin, sodium alcoholate and ethyl iodide, by using 2 molecules of ethyl iodide. Some experiments, however, indicated that an ester free from its isomeric ester was not obtained in this way. Thus, 8 grams of coumarin, 17.1 grams of ethyl iodide, 2.5 grams of sodium and 85 cc. of absolute alcohol were taken; 8.9 grams of an ester, boiling at 165° – 173° (10 mm.), were obtained. When a relatively smaller proportion of alcohol was used, and a more complete conversion of lower-melting into higher-melting isomer secured, the

resulting ester was purer. Thus, 40 grams of coumarin, corresponding amounts of ethyl iodide and sodium, and 300 cc. of absolute alcohol, yielded 53 grams of ester boiling at 172° – 174° (11 mm.). The attempt was made to isolate some of this low-melting isomer by using a larger proportion of alcohol and shortening the time of digestion. A mixture of 8 grams of coumarin, 17 grams of ethyl iodide, 2.5 grams of sodium and 100 cc. of absolute alcohol was digested for 3 hours, the alcohol was evaporated off and the neutral oil extracted with ether. The ester thus obtained yielded an acid which, when recrystallized, melted at 133° – 134° and weighed 7 grams. From the aqueous solution, on the other hand, an acid was obtained which, after recrystallization from petroleum ether, melted at 102° – 104° and weighed 1 gram. The low-melting acid was undoubtedly present, and there can, therefore, be no question but that some ethyl coumarinate was formed, in spite of the purity of the acid derived from it.

To remove the lower-boiling isomer, the crude product was saponified with boiling, concentrated, alcoholic potassium hydroxide and then boiled for 0.5 hour with a dilute aqueous solution of hydrochloric acid, which treatment converted all the low-melting isomer into higher-melting.¹ This resulting product was then converted into its ethyl ester by a 7–8 hours' digestion with absolute alcohol and a small quantity of sulphuric acid. There was very little loss in the process, and the resulting ester all distilled over at practically the same temperature. One sample came over at 176° – 176.5° (12 mm.); another at 173° – 174° (11 mm.).

Addition of Bromine to Ethylcoumarinic and Ethylcoumaric Acids and to the Ethyl Ethylcoumarate.

Perkin,² on treating methylcoumaric and methylcoumarinic acids with bromine, obtained a different dibromide from each. Ebert,³ on the other hand, found that the isomeric ethyl derivatives gave the same dibromide, and repeating the experiments of Perkin, could detect no difference between the di-

¹ Perkin : J. Chem. Soc., 39, 409.

² *Ibid.*, 39, 420.

³ *Loc. cit.* p. 157.

bromide obtained from the methyl acids. We prepared the dibromide of ethylcoumaric acid by adding bromine to the acid, each in carbon bisulphide solution and in the sunlight. The resulting acid was identical with that obtained by Ebert, melting at 155° – 156° . The dibromide of ethylcoumarinic acid was prepared in the same way, except that every precaution was taken to prevent the transformation of a low-melting into a high-melting isomer. The addition was carried on in a dark room at a temperature of 18° , and the bromine was added very slowly. Small, hard, colorless crystals were left after spontaneous evaporation of the solvent in the dark. After digesting the crystals with a little carbon tetrachloride, to remove any unchanged acid, the dried substance melted at 156° , with decomposition. The following determinations of its solubility in chloroform and carbon bisulphide, at 22° , were made:

Chloroform: 6.84 grams of solution contained 0.371 gram dibromide = 1 part of dibromide in 17.4 parts of chloroform; or in 100 parts of solution there were 5.4 parts of dibromide.

Carbon bisulphide: 8.46 grams of solution contained 0.111 gram dibromide = 1 part of dibromide in 75.6 parts of carbon bisulphide; or in 100 parts of solution there were 1.3 parts of dibromide. Ebert found the solubility to be 1.03 parts in 100.¹ These results, therefore, confirm Ebert's conclusion that the addition of bromine to ethylcoumaric and to ethylcoumarinic acid leads to the formation of the same dibromide.

The addition of bromine to the ethyl ethylcoumarate was carried out in the manner described by Perkin, except that the bromine was added only so long as decoloration took place quickly, which point was reached when about 1.9 atoms of bromine had been used. A very small quantity of hydrobromic acid was given off, indicating, perhaps, a slight substitution in the benzene nucleus. To obviate this as much as possible, the addition was always performed in diffused light, the solution of bromine in the carbon bisulphide was made dilute, the mixture kept cold and, as stated above, the ester was always kept in excess. The ease with which substitution takes place in the ring in these compounds is illustrated by the

¹ *Loc. cit.*, p. 159.

ready formation of the tri- and tetrabromides of ethylcoumaric and ethylcoumarinic acids.¹

Preparation of Ethoxyphenylpropionic Acid.

The preparation of a propiolic derivative from the dibromide of ethylcoumaric acid apparently offered little difficulty, since Perkin¹ had prepared methoxyphenylpropionic acid and Claus² ethoxyphenylpropionic acid itself in this way. Perkin removed the bromine in two stages, obtaining a monobrom acid by first rubbing the dibromide into a paste with a 50 per cent potassium hydroxide solution and then boiling the acid with alkalies. Following these directions, we invariably obtained an oil, which was insoluble in alkalies, perhaps ethoxybromstyrol or ethoxyphenylacetylene, as the chief product of the reaction, while only small quantities of the monobrom acid were found. Different alkalies in various relative proportions, at room temperature and at 0° were then tried, but without material improvement of the yield. Claus digested the dibromide immediately with boiling, concentrated potassium hydroxide and obtained a 50 per cent yield of ethoxyphenylpropionic acid. We were unable to prepare, by this method, even after prolonged digestion with the alkali, an acid which would not give a test for halogen with copper oxide. Finally, good results were obtained by adding the ester dissolved, in a little alcohol, directly to a strong, boiling solution of alcoholic potassium hydroxide and digesting the mixture for about 2 hours.

Even after such drastic treatment, followed by several recrystallizations, the final product gave the test for halogen. This may be due either to the formation of substitution products containing bromine in the benzene nucleus, in which case the bromine would not have been removed by the above treatment, or, if the monobromide of the lower-melting isomer retains its bromine with the same tenacity as does the closely related, lower melting α -monobromcinnamic acid,³ its presence would account for the persistence of the bromine in the product. The latter possibility, however, was eliminated by the

¹ *Vide* Perkin, *Loc. cit.*

² *Loc. cit.*

³ Michael and Whitehorne: *Ber. d. chem. Ges.*, **34**, 3647.

method employed in the preparation of the ester. The precautions taken to prevent substitution in the ring are mentioned above.

Our attempts to remove this trace of bromine by recrystallization proved unsuccessful. The acid may be crystallized from water, carbon bisulphide and benzene, but it is sparingly soluble in these solvents and the product is freed from the bromine in this way with difficulty. We found that conversion of the acid into the calcium salt, digestion with a small amount of 50-60 per cent alcohol and reversion into the acid, gave the best results. Samples of an acid, which repeated recrystallization from benzene and water had failed to purify, were shown to be free from halogen after a single treatment of this kind. The acid was finally recrystallized from an approximately 30 per cent mixture of acetic acid and water, which treatment, however, is accompanied with considerable loss.

The yield of crude acid was usually good, amounting to from 75-90 per cent of the theory. The yield of pure acid was never greater than 50 per cent, the chief loss occurring in the final recrystallization. Pure potassium hydroxide and alcohol should be used for the digestion, otherwise the resulting acid will only solidify after a long time. Prolonged digestion, too, decreases the purity of the product. The melting-point of the acid given by Ebert is 114° . Our purest samples melted at $115^{\circ}.5-116^{\circ}$.

Action of Hydrobromic Acid on Ethoxyphenylpropionic Acid.

Nine and eight-tenths grams of *o*-ethoxyphenylpropionic acid were added to 85 grams of fuming hydrobromic acid, in a bath of ice water. After standing over night, the mixture was filtered, and the precipitate washed with ice water. The product of the reaction was dissolved in warm, 70 per cent alcohol, and small quantities of alcohol were added until the acid came down crystalline instead of as an oil. The first crop of crystals weighed 7.8 grams, the second 2.5 grams. They melted at $119^{\circ}-119^{\circ}.5$.

The product is easily soluble in alcohol, ether, acetic acid and hot carbon tetrachloride, slightly in cold carbon tetrachlo-

ride and difficultly soluble in water. After recrystallizing from acetic acid once and from carbon tetrachloride twice, it melted at 120° . Analysis:

0.1100 gram bromide gave 0.0768 gram AgBr.

	Calculated for $C_{11}H_{13}O_3Br$.	Found.
Br	29.72	29.50

It is, therefore, ethylbromcoumaric acid, with the bromine undoubtedly in the β -position to the carboxyl group.

The filtrate from the crude ethylbromcoumaric acid was allowed to stand several days and then diluted with water. A yellowish precipitate was obtained, weighing but a few tenths of a gram, which was difficultly soluble in carbon bisulphide and carbon tetrachloride, chloroform, benzene and ligroin; somewhat soluble in hot water, easily in alcohol, acetic acid and especially soluble in acetone.

A sample of this product was recrystallized three times from boiling water. Small, yellowish white, needle-shaped crystals were obtained, which contained no halogen. They were again recrystallized from a mixture of acetone and ligroin, b. p. 110° – 120° . The greater part of the acetone was then driven off by heating, whereupon the substance separated out in fine, white needles. It melts at 211° – $212^{\circ}.5$ and, since it dissolves in alkalies, must be acidic in character. The solutions in alkalies thus obtained were colorless and the substance cannot, therefore, be coumaric acid. Analysis:

	Calculated for $C_{10}H_{11}O_3$.	Found.
C	67.00	67.07
H	6.20	6.53
O	26.80	26.40

These results correspond, however, to no substance which might be expected in the reactions.

The Reduction of β -Bromalloethylcoumaric Acid.

The reduction of β -bromallocinnamic acid to allocinnamic acid is best effected by means of zinc dust suspended in alcoholic solution of the acid, as described by Liebermann and

Scholtz.¹ The product of the reactions is a mixture, consisting mainly of the zinc salt of allocinnamic acid, some ordinary cinnamic acid and of a very low melting acid.

The allo acid is removed by taking advantage of the marked insolubility of its aniline salt in ligroin. Erlenmeyer sen.² isolated the iso acid by fractional precipitation and recrystallization from ligroin; Michael and Whitehorne,³ by means of the different solubilities of the barium salts of the 3 acids in methyl alcohol.

Since the reduction of bromalloethylcoumaric acid might lead to a similar mixture of isomeric acids, experiments were carried out to see whether the methods of separation employed with the mixtures of the cinnamic acids could be used here. The action of aniline on ethylcoumaric and ethylcoumarinic acids was studied and the solubilities of the barium and calcium salts of these acids in water, ethyl alcohol and methyl alcohol were determined. The solubilities of the barium and calcium salts of ethylmellilotic acid, or hydroethylcoumaric acid, in the same solvents were also determined; since Michael and Garner⁴ have concluded that the isocinnamic acid, obtained by the reduction of the β -brom acid, may be a mixture of allocinnamic acid and hydrocinnamic acid.

Aniline, in benzene solution, has no apparent action on ethylcoumaric or ethylcoumarinic acids, either at room temperature or at 100°.

For the solubility determinations, the barium and calcium salts were prepared by digestion of the acids with pure barium and calcium carbonates. Ethylmellilotic acid was prepared from ethylcoumaric acid by reduction with sodium amalgam. The salts were recrystallized either from water or alcohol. The temperature was allowed to vary between 20° and 24°, since great accuracy was not necessary.

It should be remarked that supersaturated solutions of these salts are easily formed, especially if they are in an amorphous condition, such for instance as a gummy residue, obtained by

¹ Ber. d. chem. Ges., **25**, 950.

² Ann. Chem. (Liebig), **287**, 5.

³ Ber. d. chem. Ges., **34**, 3648.

⁴ *Ibid.*, **36**, 900.

evaporating the solution of a salt in a solvent in which the salt is very soluble.

	Solubility of the barium salts of		
	Ethylcoumarinic acid.	Ethylcoumaric acid.	Ethylmellilotic acid.
In water	(1) 2.7 (2) 2.8	(1) 290 (2) 226	(1) 18.6 (2) 19.9
Methyl alcohol	(1) 414 . . .	(1) 30.4 (2) 22.4	(1) 31.4 . . .
Ethyl alcohol	(1) 2137 (2) 2327 . . .	(1) 259 (2) 110 (3) 167	(1) 104 (2) 86.3 (3) 93.0

	Solubility of the calcium salts of		
	Ethylcoumarinic acid.	Ethylcoumaric acid.	Ethylmellilotic acid.
In water	(1) 18.7 (2) 31.7	(1) 219 . . .	(1) 147 . . .
Methyl alcohol	952	861	205
Ethyl alcohol	(1) 731 (2) 1454 . . .	(1) 1641 (2) 1892 (3) 1846	1121 . . .

The figures indicate parts by weight of solvent corresponding to a single part of solute.

It is evident that alternate treatment of the barium salts of ethylcoumaric, ethylcoumarinic and mellilotic acids, with water and alcohol, should offer a method of separation.

Four reduction experiments were carried through, with nearly identical results, using Liebermann's method. In the first of these experiments 8 grams of ethylbromcoumaric acid, 16 grams of zinc dust and 80 cc. of 96 per cent alcohol were taken. The mixture was digested for 6 hours on the water-bath. At frequent intervals samples of the mixture were removed and the zinc bromide determined, in order to ascertain the progress of the reaction. Since these tests showed that the reaction was complete within the first half hour, in our later experiments the period of digestion was shortened to an hour. The mixture was then diluted with an equal volume of water and evaporated to a small bulk; more water was added, the solution acidified and the acid extracted with ether. It softened at 75° and melted at 81°-97°, being evidently a mixture, apparently containing ethylcoumarinic acid, m. p. 103°.

It seemed advisable, therefore, to follow the method of separation suggested above, depending on the different solubilities of the barium salts of the ethyl derivatives of coumaric, coumarinic and mellilotic acids. The crude product was converted into the barium salts by prolonged digestion for 8-10 hours with barium carbonate, in water, at 70°. The resulting solution was filtered and the filtrate evaporated to dryness. The residue was then extracted with about 50 cc. of absolute alcohol, in which barium ethylcoumarinate is very insoluble. At first it goes into solution, but quickly comes down as a copious, white substance. The mixture was allowed to stand over night, to insure precise saturation, and then filtered. Two samples of the precipitate were dissolved in water, the solution acidified and the acid extracted with ether. As they melted between 99° and 102° they were evidently slightly impure ethylcoumarinic acid. The yield, too, was considerable. In this experiment the weight of the barium ethylcoumarinate was 6.8 grams, while in another, starting with the same amount of ethylbromcoumaric acid, 7.3 grams of barium salt were obtained, corresponding, respectively, to a yield of 80 and 90 per cent of ethylcoumarinic acid.

Ethylcoumarinic acid is, therefore, the main product of the reduction of β -ethylbromcoumaric acid by means of zinc dust in alcoholic solution.

The Existence of Isocoumaric Acid.

It remained to detect, if possible, the presence of an acid corresponding to the isocinnamic acid of Erlenmeyer and Michael and Whitehorne, this being the second object of the research. It was evident, from the purity of the ethylcoumarinic acid which had been isolated from the product of reduction in the above experiment, that the iso acid must, if present at all, be dissolved in the filtrate from the barium ethylcoumarinate. Further, from analogy with allobromcinnamic acid we also should expect that the reduction would lead to the formation of some of the high-melting isomer, or ethylcoumaric acid. The alcoholic filtrate from the barium ethylcoumarinate was evaporated to dryness and extracted

with about 10 cc. of water, in which barium ethylcoumarate had been found to be difficultly soluble. The mixture was allowed to stand over night and was then filtered. A portion of the gummy residue from the evaporation of this filtrate was dissolved in much water and acidified. The free acid was extracted with ether and dried, when it melted at 127° – 132° . There can be no doubt but that it was fairly pure ethylcoumaric acid, m. p. 133° . The exact weight of the acid was not easy to determine because of its gummy nature, but it was approximately 0.3 gram, or 5 per cent of the total reduction product.

Any iso acid must have been dissolved in the filtrate from the barium ethylcoumarate. It would have been mixed, however, with as much barium ethylcoumarinate and ethylcoumarate as 50 cc. of absolute alcohol and 10 cc. water, in succession, would have dissolved. The filtrate was evaporated to dryness and the residue, amounting to about 0.3 gram, extracted with 5 cc. of each solvent, in succession, whereby some ethylcoumarinic and a little ethylcoumaric acid were further separated. The aqueous solution remaining from this last extraction was filtered and acidified. The precipitated acid was filtered off and dried. The melting points of samples of the acid thus extracted in the 4 reduction experiments were as follows:

- | | | | |
|-----|----------------------------|-----------------------|------------------------------------|
| (1) | softened at 83° , | ran at 87° , | completely melted at 115° |
| (2) | " " 82° , | " " 92° , | " " " 101° |
| (3) | " " 79° , | " " — | " " " 86° |
| (4) | " " 80° , | " " 94° , | " " " 120° |

The weight of the residue obtained from the reduction of 8 grams of ethylbromcoumaric acid varied between 0.1 and 0.2 grams, or 2–3 per cent of the total reduction product.

These melting points indicated that the residue was a mixture of ethylcoumaric and ethylcoumarinic acids. The results with the third portion, however, suggested that a still lower melting acid might be present. To be better able to judge regarding this possibility, the melting points of various mixtures of (1) ethylcoumaric and ethylcoumarinic acids, (2) ethylcoumaric and ethylmellilotic acids, (3) ethylcoumarinic and

ethylmellilotic acids were determined. These mixtures were prepared by dissolving the acids either in absolute methyl or ethyl alcohol and evaporating to dryness. The point at which the substance ran freely could be determined with the greatest accuracy of any. Ethylmellilotic acid was included because the presence of its analogue had been suspected among the reduction products of allocinnamic acid.¹

Table I.—*Mixtures of Ethylmellilotic and Ethylcoumaric Acids.*

Weight of mixture. Gram.	Total weight of ethylcoumarinic acid added. Gram.	Percentage of ethylmellilotic acid.	Mixture.		
			Softened.	Ran.	All melted.
0.4676		100			
0.5270	0.0594	88.7	62°	66°	74°
0.5687	0.1031	81.9	62°	70°	77°
0.6211	0.1575	74.6	60°	66°	70°
0.7221	0.2605	63.9	59°	61°.5	70°
0.8107	0.3511	56.7	60°	62°.5	70°
Total weight of ethylmellilotic acid added.					
0.6373					
0.7108	0.0735	10.3	72°	86°	101°
0.8282	0.1951	23.3	63°	86°	96°
0.9044	0.2713	30.2	62°	71°	98°
1.0637	0.4326	40.6		64°.5	87°
1.1826	0.5535	46.8	60°	62°.5	82°
Total weight of ethylcoumarinic acid.					
0.1044					
0.1070	0.0026	97.6	69°	77°.5	79°.5
0.1117	0.0093	91.7	61°	77°.5	78°
0.1160	0.0156	86.6	58°	69°	75°
0.1226	0.0242	80.3	61°	63°	65°
0.1276	0.0254	80.1	61°	64°.5	71°

¹ Liebermann: Ber. d. chem. Ges., 36, 179. Michael and Garner: *Ibid.*, 36, 907.

Table II.—Melting Points of Mixtures of Ethylcoumaric and Ethylcoumarinic Acids.

Weight of mixture. Gram.	Total weight of ethylcoumaric acid added. Gram.	Percentage ethylcoumaric acid.	Mixture.		
			Softened.	Ran.	Completely melted.
0.2029		0.0			
0.2219	0.0190	8.58	83°.5	92°.5	100°.5
0.2385	0.0186	15.7	86°	91°	98°
0.2599	0.0234	23.2	83°	84°	91°
0.2725	0.0146	27.4	82°	84°	90°
0.3090	0.0385	36.9	81°	84°	101°
0.3726	0.0656	48.2	82°	85°.5	112°
Total weight of ethylcoumarinic acid added.					
0.2444		100.0			
0.2518	0.0074	97.1	117°	128°	131°
0.2820	0.0302	86.7	102°	115°.5	127°
0.3020	0.0220	80.3	89°	115°	126°
0.3536	0.0536	68.0	83°	97°	126°
0.4044	0.0528	58.9	83°	89°	117°
0.4262	0.0738	49.6	84°	85°.5	107°

Melting Point of Mixture of Ethylcoumaric and Ethylmellilotic Acids.

Weight of mixture. Gram.	Total weight of ethylmellilotic acid added. Gram.	Percentage ethylmellilotic acid.	Mixture.		
			Softened.	Ran.	Completely melted.
0.1817		0.0			
0.1950	0.0133	6.8	110°	126°	129°
0.2062	0.0265	12.8	117°	124°	129°
0.2283	0.0506	22.2	100°	118°	129°
0.2588	0.0831	32.1	75°	105°	118°
0.2841	0.1104	39.6	77°	95°	106°.5
0.3101	0.1384	44.6	71°	77°	114°
Total weight of ethylcoumaric acid.					
0.1562		100.0			
0.1723	0.0161	90.7	72°	74°.5	76°.5
0.1887	0.0345	81.6	70°.5	72°	73°
0.2081	0.0559	73.2	70°.5	72°.5	95°
0.2422	0.0920	62.0	73°	86°	107°
0.2688	0.1206	55.2	75°	88°.5	110°
0.3077	0.1615	47.5	71°	96°.5	119°

When these results were plotted in the form of curves it is found that all the melting points of the above residues fit the melting point curve for mixtures of ethylcoumaric and ethylcoumarinic acids. The conclusion that the residue consisted of these 2 acids is thus confirmed, but it was desirable, if possible, to apply a more delicate test for the detection of ethylmellilotic acid. This available residue was too small and undoubtedly too impure to afford an analysis sufficiently accurate to distinguish between ethylcoumaric and ethylmellilotic acids. The action of potassium permanganate on a mixture of these two acids was tried, and although the unsaturated acid oxidized much more rapidly, the end point was so difficult to ascertain that the method was abandoned. The following experiments on the action of bromine vapor on ethylcoumaric, ethylcoumarinic and ethylmellilotic acids were carried out in the hope of obtaining some method of detecting small quantities of the ethylmellilotic acid in the presence of the other three.

Action of Bromine, in Excess, on Ethylcoumarinic, Ethylcoumaric and Ethylmellilotic Acids.

(1) *Ethylcoumarinic Acid*.—Samples of this acid were exposed to the action of bromine vapor in a desiccator, kept in the dark. After 24 hours the excess of bromine was allowed to diffuse into the air and the remainder removed by placing the product over sodium hydroxide and sulphuric acid, in a vacuum.

(1) 0.3579 gram acid increased 0.5239 gram, or 323.2 equivalents.

(2) 0.2370 gram acid increased 0.3535 gram, or 320.7 equivalents.

4 atoms of Br — 2 atoms H = $320 - 2 = 318$ equivalents.

No further diminution in weight occurred even after prolonged standing over sodium hydroxide.

The solubilities of this bromide agree with those of the bromide derived from ethylcoumaric acid, although we did not succeed in recrystallizing it. The crude product softened at 142° and melted at 150° – 152° . Analysis:

0.2062 gram substance yielded 0.2894 gram AgBr.

	Calculated for $C_6H_2Br_2OC_2H_5 \cdot C_2H_2Br_2COOH$.	Found.
Br	62.64	59.7

(2) *Ethylcoumaric Acid*.—Exposed over night to the action of bromine vapor, the substance increased in weight by an amount equivalent to between 3 and 4 atoms of bromine, and lost weight but very slightly on further exposure over sodium hydroxide. Protracted exposure to bromine vapor resulted in the addition of somewhat more than 4 atoms, but the product lost weight over sodium hydroxide until the increment of bromine corresponded to about 3.5 atoms. The addition product is very soluble in acetone, alcohol, ether, and carbon bisulphide; easily soluble in hot, less soluble in cold benzene, toluene and chloroform; somewhat soluble in hot ligroin, but decomposes more or less if the ligroin employed boils much above 100° . A sample was recrystallized from a mixture of acetone and ligroin, then several times from toluene and chloroform, when it melted at 183° – 184° , with very slight decomposition. It crystallized from toluene and ligroin in thin, rhombic plates. Analysis:

0.2263 gram substance yielded 0.3374 gram AgBr.

	Calculated for $C_6H_2Br_2OC_2H_5 \cdot C_2H_2Br_2COOH$.	Found.
Br	62.64	63.45

The substance may be called α, β -dibrom- β -dibromethoxy-phenylpropanic acid.

(3) *Ethylmellilotic Acid*.—The acid, when exposed to bromine vapor, is converted into a thick, red liquid. The increase in weight corresponds, roughly, to 4 atoms of bromine. However, on standing over sodium hydroxide the greater part of this bromine was given off and a steady loss in weight occurred.

It appears, then, that these 3 acids do not behave at all identically toward bromine vapor. While the 2 unsaturated acids form dry, powdery addition products, which are apparently mixtures of tri- and tetrabrom addition products, and which do not lose in weight on standing over sodium hydrox-

ide after the excess of bromine has been removed, ethylmellilotic acid forms a thick liquid which loses in weight indefinitely under these same conditions. It was found possible to detect, in this way, a small per cent of ethylmellilotic acid in mixtures of it with ethylcoumaric and ethylcoumarinic acids.

It follows, then, that if the final residue from the reduction experiment contained more than a small per cent of ethylmellilotic acid, the external appearance of the addition product with bromine, combined with a steady loss in weight on standing over sodium hydroxide would disclose the fact. A sample of the residue was, therefore, exposed over night to the action of bromine vapor. It yielded an addition product which was dry and powdery.

After treatment with bromine and 2 hours' standing over sodium hydroxide, 0.0678 gram of residue weighed 0.1731 gram; after standing 16 hours longer, it weighed 0.1733 gram. The increment equals 0.1053 gram, and corresponds to an equivalent increment of 297.2, or somewhat less than 4 atoms of bromine, as would be expected from a mixture of ethylcoumarinic and ethylcoumaric acids. As no loss in weight occurred we may conclude that certainly not more than minute quantities of ethylmellilotic acid could have been formed in the reduction.

Action of Four Equivalents of Bromine on Ethylcoumaric and Ethylcoumarinic Acids.

(1) *Ethylcoumarinic Acid*.—Three grams of pure, dry acid were dissolved in chloroform, and to the solution 4.5 grams, = 4 atoms, of bromine, also dissolved in chloroform, were added. The mixture was allowed to stand several days in the dark. Much hydrobromic acid was evolved and the solution finally became colorless, a considerable quantity of white crystals being deposited.

A small quantity of a thick, heavy, red liquid was also formed, which gave off fumes of hydrobromic acid on exposure to the air. The supernatant liquid was allowed to evaporate in the air and a residue was obtained, which appeared to be identical with the crystalline product. The crystals are very easily soluble in acetone and alcohol, quite soluble in boiling

toluene and rather difficultly soluble in chloroform, carbon tetrachloride and, especially, in ligroin. When crystallized from a mixture of acetone and ligroin, then from toluene and, finally, from chloroform, it melts at 182° – 183° , with considerable decomposition. The crystals from the mixture of acetone and ligroin were short, slightly rhombic needles; from toluene they were small, colorless and nearly rectangular in shape. Analysis:

0.1621 gram substance yielded 0.2101 gram AgBr.

	Calculated for $C_8H_3BrOC_2H_5, C_2H_2Br_2COOH.$	Found.
Br	55.66	55.15

The substance may be called α, β -dibrom- β -bromethoxy-phenylpropanic acid.

(2) *Ethylcoumaric Acid*.—Three grams of pure, dry acid were dissolved in chloroform, and to it 4.5 grams, or 4 equivalents of bromine, also dissolved in chloroform, were added. After standing several days the solution was still reddish in color, and no crystals had formed, though much hydrobromic acid had been given off. On evaporation a residue was left which proved to be about as soluble in carbon tetrachloride as it was in chloroform; otherwise it closely resembled in its solubilities the above tribrom compound of ethylcoumarinic acid. It gave gummy residues, however, from nearly every solvent, and could not be recrystallized.

To enable us to draw some conclusion relative to the composition of this residue it was treated with alkalies. One gram of the residue, dissolved in a little alcohol, was added to a boiling solution of 1.5 grams of sodium hydroxide in 15 cc. of alcohol, and the mixture was digested on the water-bath for 1.5 hours. The solution was then evaporated, the residue dissolved in water, an oily turbidity filtered off, and the filtrate acidified. The resulting flocculent precipitate was filtered off and dried. It crystallizes in needles and is easily soluble in acetone, alcohol, chloroform, carbon tetrachloride, carbon bisulphide and toluene; difficultly soluble in ligroin and water.

After 2 recrystallizations from toluene the substance melted at 134° – 136° . Analysis :

0.0957 gram substance gave 0.0662 gram AgBr.

	Calculated for $C_6H_3BrOC_2H_5.C_2COOH.$	Found.
Br	29.50	29.44

This substance is, therefore, *o*-ethoxybromphenylpropionic acid.

The formation of this monobrom acid showed that a bromine atom had entered into the benzene nucleus and that the above residue must have consisted principally of a tribrom derivative of ethylcoumaric acid, or *o*-ethoxybromphenyldibrompropionic acid. Further, it is significant, that its properties are decidedly different from those of the *o*-ethoxybromphenyldibrompropionic acid derived from ethylcoumarinic acid, although the possibility of stereoisomerism disappeared with the unsaturation.

Since, however, Perkin found that methylcoumaric and methylcoumarinic acids gave the same *o*-methoxybromphenyldibrompropionic acid, this indirect evidence of the dissimilarity of the corresponding products derived from the ethyl acids requires confirmation.

Addition of Chlorine to Ethylcoumarinic Acid.

Two grams of ethylcoumarinic acid were added to a sufficient quantity of a 9.2 per cent solution of chlorine, in carbon tetrachloride, to form a dichloride. The acid had previously been dissolved in dry carbon bisulphide and the addition was carried on in the dark. After standing 12 hours crystals had separated, and these were filtered off. They melted at 127° – 128° and softened at 125° . They were easily soluble in alcohol, chloroform and hot carbon tetrachloride ; somewhat soluble in ligroin and carbon bisulphide. After recrystallization from ligroin the substance melted at 130° – 131° . Analysis :

0.1559 gram substance gave 0.1720 gram AgCl.

	Calculated for $C_6H_4OC_2H_5.C_2H_2ClCOOH.$	Found.
Cl	26.96	27.23

The Conversion of Coumarinic Derivatives into Their Coumaric Isomers.

Coumarin is converted into the sodium salt of coumaric acid by boiling with strong, aqueous sodium hydroxide,¹ more readily by boiling with a solution of sodium ethylate in absolute alcohol. Coumaric acid is reconverted into coumarin with so much difficulty that it would seem probable that the latter is the lactone of an allocoumaric acid. It seemed of interest, therefore, to subject ethylcoumarinic acid to the same treatment. Three-tenths gram of sodium was dissolved in 6 cc. of absolute alcohol, and to the solution 1 gram of pure ethylcoumarinic acid was added, and the mixture was digested in an oil-bath, at 120°, for 5 hours. The solution was then diluted with water, evaporated to dryness, the residue dissolved in water and acidified. The resulting acid, when dried, melted at 98°–100°. This experiment was repeated, except that 4 instead of 6 cc. of absolute alcohol were employed, whereupon the resulting acid melted at 99°–102°. It is evident that ethylcoumarinic acid is not affected by digestion with a solution of sodium in absolute alcohol.

Perkin² found that methylcoumarinic acid is converted into its isomer by boiling with dilute mineral acids. Ethylcoumarinic acid was found to be similarly changed. The conversion, however, is slow. Thus 0.5 gram of acid, after heating with 10 cc. of dilute hydrochloric acid for 1.25 hours, in an oil-bath, at 120°, melted between 104° and 122°, corresponding to about 75 per cent of ethylcoumaric acid (see table, p. 573). On the other hand, coumarin was quite unchanged by this treatment.³

Liebermann⁴ has found that allocinnamic acid is converted rapidly into ordinary cinnamic acid by the action of iodine, dissolved in carbon bisulphide. This experiment was tried with ethylcoumarinic acid. One and one-half grams of the acid, m. p. 103°, were added to a solution of 3 grams of iodine in

¹ Delalande : Ann. Chem. (Liebig), 45, 332. Perkin : J. Chem. Soc., 31, 417. Fittig and Ebert : Ann. Chem. (Liebig), 216, 142.

² Loc. cit., p. 410.

³ Delalande : Loc. cit., p. 333.

⁴ Ber. d. chem. Ges., 23, 2512.

35 grams of carbon bisulphide, and the mixture digested for 4.5 hours on the water-bath. The iodine was removed by means of a strong solution of sodium thiosulphate and the colorless carbon bisulphide solution was then shaken with water and, finally, with an aqueous solution of potassium hydroxide. From the alkaline solution an acid was obtained which melted at 132° – 133° , showing a complete conversion into ethylcoumaric acid.

For comparison, the effect of iodine on coumarin itself was tried. A quantity of coumarin, with 10 times its weight of water, was digested 2.5 hours with a solution of iodine in carbon bisulphide, without any change taking place.

It is also of interest that, although coumarin is rapidly converted into orthocoumarinate by boiling with a strong solution of sodium alcoholate in *absolute* alcohol, it is scarcely affected at all if a solution of the alcoholate in 96 per cent alcohol be employed. This fact agrees with the experience gained in the preparation of ethylcoumarinic acid, and may also explain the difficulty which Miller and Kinkelin¹ experienced in converting coumarin into coumaric acid.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XII.—STUDIES ON THE SOILS OF THE NORTHERN PORTION OF THE GREAT PLAINS REGION : THE SECOND STEPPE.

BY FREDERICK J. ALWAY.

Very little study has been devoted to the chemical and physical properties of the soils of the northern portion of the great plains region, better known as the Canadian Northwest. In the few investigations that have been conducted there, methods have been employed which are adapted to the humid climate of eastern Canada, but which are ill suited to the conditions that have produced the prairies and plains.

The commonly accepted explanation of the large yields of grain obtained in the Canadian Northwest is quite erroneous and obscures the value, to the agricultural interests of the

¹ Ber. d. chem. Ges., 22, 1714.

semi-arid portions of the United States, of the data contained in the annual reports of the Indian Head Experimental Farm, covering a period of 17 years.

The yield from a given area of crop depends upon the climate during the season of growth and upon the fertility of the soil, whether it is considered that the latter is due chiefly to its physical properties or to its store of readily available plant food. The different factors of climate are easily determined and their influence upon plant growth is very apparent, while the relative fertility of the soil can be ascertained only by measuring the crop yield under ideal climatic conditions, which differ for different soils. The climate of the second prairie steppe of Canada is distinguished from that of the prairie portions of the United States chiefly in its lower winter temperature, its somewhat longer summer days and its low precipitation, the rainfall occasionally amounting to less than 5 inches during the crop season. Eminent American and English chemists have advanced, or accepted, in explanation of the large yields of grain in this region, the theory that the frost penetrates to a great depth during the winter and, during the summer months, furnishes a constant supply of moisture to the growing grain. Sir Wm. Crookes¹ has made the statement that "The fertility of the Northwest Provinces of the Dominion of Canada is due to an exceptional and curious circumstance. In winter the ground freezes to a considerable depth. Wheat is sown in the spring, generally April, when the frozen ground has been thawed to a depth of 3 inches. Under the hot sun of the short summer the grain sprouts with surprising rapidity, partly because the grains are supplied with water from the thawing depths. The summer is too short to thaw the ground thoroughly, and gate posts or other dead wood extracted in the autumn are found still frozen at their lower ends." Storer² quotes, as an illustration of how melting ice may serve as a useful store of moisture in certain situations and for certain crops, in regard to Assiniboia, "that even in late July some of the soil still holds the winter's frost at a depth of several

¹ Presidential Address, British Assoc. Report, 1898, p. 8.

² Agriculture (7th ed.), Vol. I., p. 144.

feet below the surface. This underground layer of frozen earth is believed to explain the wonderful fertility of the soil, as the frost, in gradually coming to the surface during the summer months, creates a moisture which, meeting the warmth from above, forms a kind of natural hot bed. This moisture counteracts the scarcity of rain during the spring and summer and accounts for the grain being forced with such amazing rapidity after the late sowing."

Up to the present time this explanation seems to have passed without criticism. The soil of the prairie and of the grain fields does not remain frozen throughout the summer at any depth in ordinary years and, probably, in any year. The experimental data upon which this generalization is based will be published in another journal. The preponderating importance of the nature of the subsoil, rather than that of the surface soil, or of the depth to which the frost penetrates, has hitherto not been recognized.

At the southern boundary of Canada the region of plain and prairie extends from the 96th to the 114th meridian and "narrows rapidly northwards, by the encroachment of its eastern border, but continues as a great physical feature to the shore of the Arctic Ocean. Beyond the North Saskatchewan River, however, it loses its essentially prairie character and becomes, with limited exceptions, thickly covered with coniferous forest."¹ The Rocky mountains or bordering foothills form the western boundary of this interior continental plateau; the northeastern boundary is formed by the rocky plateau of the great Archaean nucleus of the continent. Two escarpments, which hold a northwest and a southeast course across the plains, form the eastern boundaries of the third and the second prairie levels or steppes, the more easterly of which overlooks the lowest or first steppe. The three prairie steppes differ in age, in the character of the superficial deposits and, to a considerable extent, in climate.

The first steppe, a large part of which is commonly known as the Red River Valley, extends from the Red River and

¹ Selwyn and Dawson: "Descriptive Sketch of the Physical Geography and Geology of the Dominion of Canada," 1884, p. 27.

Lake Winnipeg westward to the first escarpment which, in its different portions, passes under the designations—Pembina Mountain, Tiger Hills, Riding Mountain, Duck Mountain, Porcupine Hills and Pasquia Hills. This prairie level was covered, toward the close of the glacial period, by a large body of fresh water, named by Upham,¹ Lake Agassiz. The surface soil, which is of lacustral origin, consists of fine silty material over the greater portion of the steppe, the average height above the sea being about 800 feet. The Red River Valley of Minnesota and North Dakota forms a southward extension of this area. The soil of this valley, which is famous for its fertility, has been studied at the experiment stations of the 2 states mentioned. The attention of Lawes and Gilbert was drawn to the fertility of the Manitoba portion and they made analyses of samples from various localities. Some contributions to the chemistry of the soil of this steppe have since been made by Shutt.²

The second steppe extends from the first escarpment to the second, the Missouri Couteau. "It includes the whole eastern portion of the great plains, properly so-called, of Canada."³ The average altitude of this prairie level is about 1600 feet. Its climate, like that of the first steppe, is characterized by warm summers, very cold winters and a low winter precipitation. The rainfall, which occurs chiefly during the growing season, is lighter than that of the first level. Considerable areas of the second steppe were covered by lakes at the time that Lake Agassiz occupied the lowest level, and in these deposits of silty material of varying thickness were formed.

The fertility of the soil of the second steppe is apparent to any one that visits the province of Saskatchewan at the close of a favorable crop season. It is a well-recognized fact, however, that in regions where the normal precipitation is very small, abundant crops are produced, even on very coarse sands, in those seasons during which the rainfall is unusually heavy and well distributed. Evidence that the soil of southern Sas-

¹ W. Upham : Lake Agassiz, U. S. Geol. Survey, 1895.

² Annual Reports Canada Expt. Farms.

³ Selwyn and Dawson : *Loc. cit.*

katchewan is characterized by the ability to produce a high average yield of wheat, oats, barley and potatoes for many years in succession, without the application of any fertilizers, or even the growing of leguminous crops, is furnished by the annual reports of the Indian Head Experimental Farm, which has been maintained by the Canadian government since 1888. Experimental farms are maintained by the same government at 4 other places, Nappan in Nova Scotia, Ottawa in Ontario, Agassiz in British Columbia, and Brandon in Manitoba. The 3 represent humid climates with a heavy winter precipitation, while the farms at Brandon and Indian Head are in the region of very light winter precipitation. In illustration of the above-mentioned characteristics the yields of the 12 best adapted varieties of wheat, oats, barley and potatoes, during the past 4-9 years that they have been under trial at the 5 farms, where the conditions of experiment are similar, are given in Table I. The average yield of each of these 4 crops is higher at Indian Head than at any of the 4 other experimental farms. The yields of the same crops in 1901 are given in the table in illustration of the effect of a very favorable crop season at Indian Head. It is important to note that only in the case of peas, in addition to the 4 crops mentioned, does the Indian Head farm give heavy yields. The other crops indicated in the table, as well as hay, produce more heavily at each of the 4 other farms.

The soil of the Indian Head farm is typical of that of the greater portion of the second steppe. The surface soil consists in some places of boulder clay and in others of a lacustral deposit of clay overlying the till. In none of the fields on the farm, where borings were made by the writer, was the lacustral deposit found to exceed 3 feet in depth. The soil of the whole of the second steppe is of glacial origin, the till, which covers the underlying Cretaceous shales, varying in depth from a few feet in the vicinity of the Souris river to more than 200 feet over a great part of the area. The drift consists of an intimate mixture of the country rock, in a very finely divided condition, with powdered Devonian and Silurian limestones, together with material from the great Archaean

Table I.

Average yields of the best adapted varieties of various crops at the 5 Canadian Experimental Farms. Some of the varieties included in the averages have been under trial only 4 years, but most of them have been tested for 9 years.

Crop.	No. of varie- ties.	Average for the years 1895-1903. ¹					Average of the same number of varieties at Indian Head in 1901. ²
		Average for 5 farms.	Ottawa.	Nappan.	Brandon.	Indian Head.	
Oats, bush. (34 lbs.)	12	76.2	64.5	77.2	88.5	94.5	67.5
Barley, 2-rowed, bush.	6	45.5	45.3	45.1	46.0	56.2	43.3
" 6-rowed, "	6	50.8	50.1	50.6	56.0	60.5	45.9
Spring wheat, "	12	34.3	28.0	36.9	35.9	42.2	34.9
Peas	12	35.7	33.6	31.9	47.3	41.5	37.5
Maize, green, tons	6	19.4	23.1	18.8	19.6	14.6	22.9
Turnips,	6	31.5	34.2	39.9	25.1	22.3	39.7
Mangels,	6	31.7	39.1	38.0	31.1	22.6	34.3
Carrots,	6	22.0	30.7	22.3	14.3	12.2	31.1
Sugar beets,	4	24.5	28.8	27.2	19.4	11.2	17.0
Potatoes, bush.	12	377.9	399.2	387.0	395.3	433.6	371.0
							620.5

¹ Bull. 48, Canad. Expt. Farms (1904).

² Bull. 39, Canad. Expt. Farms (1901).

area to the northeast. The gravel, stones and boulders are chiefly from the last-mentioned source, together with a limited number composed of limestone, these, probably, having been brought from the Palaeozoic belt separating the Cretaceous area from the Archaean.

Previous Analyses of Soils from the Second Steppe.

The only analyses of soils from this prairie level hitherto published are those by Shutt.¹ For purposes of comparison these are given.

Table II.—Analyses of Soils, Water-free, from the Northwest Territories.

	Moosomin. Surface.	Saltcoats. Surface.	Yorkton. Surface.	Yorkton. Subsoils.
Potash	0.36	0.34	0.49	0.42
Phosphoric acid	0.11	0.21	0.21	0.09
Lime	0.95	2.90	0.06	0.75
Nitrogen	0.48	0.57	0.50	0.13
Loss on ignition	11.79	13.57	14.01	8.18

The depth to which the samples were taken is not stated.

Chemical Analysis of Indian Head Soils.

The samples of soil, the chemical analysis of which is given in Table III., were secured by Mr. B. F. Reynolds on Nov. 11, 1904, from a field of 10 acres on the Indian Head farm that had never been fertilized. The field was in fallow in 1904 and in 1905 bore a crop of spring wheat, yielding an average per acre of 46 bushels and 54 pounds. The soil from each foot section was removed by means of an auger, carefully sampled, all stones being rejected, and then air-dried. A 5 lb. sample of each foot section was sent by express to the writer. The portion of the soil that passed through a 0.5 mm. sieve was dried at 100° and digested with hydrochloric acid, sp. gr. 1.115, at the temperature of boiling water, for 10 hours.

The percentage of nitrogen seemed so low in comparison with the results of Shutt's analyses that the writer personally took samples from the same field in September, 1905. The nitrogen in this sample from the first foot amounted to 0.25

¹ Report Canad. Expr. Farms, 1897, p. 164.

Table III.—*Chemical Analysis of Indian Head Soils.*

	First foot.	Second foot.	Third foot.	Fourth foot.	Fifth foot.	Sixth foot.
Insoluble material	74.18	63.42	65.46	70.19	70.03	69.99
K ₂ O	0.37	0.37	0.41	0.60	0.40	0.42
Na ₂ O	0.34	0.31	0.37	0.27	0.36	0.28
CaO	1.35	10.12	9.67	7.60	7.02	7.08
MgO	1.45	3.14	3.33	2.97	3.32	3.27
Mn ₂ O ₄	0.07	0.07	0.09	0.06	0.11	0.12
Fe ₂ O ₃	3.94	2.98	2.80	2.79	3.06	3.40
Al ₂ O ₃	6.71	4.30	4.35	3.39	4.02	3.54
P ₂ O ₅	0.17	0.14	0.14	0.17	0.16	0.18
SO ₃	0.06	0.03	0.07	0.08	0.43	0.09
CO ₂	0.46	9.51	9.93	8.00	7.57	7.13
Volatile matter	10.87	5.52	3.45	3.03	3.78	3.64
Total	99.97	99.91	100.07	99.15	100.26	99.14
Nitrogen	0.23	0.10	0.04	0.04	0.04	0.04
Hygroscopic coefficient	10.7	6.5	6.3	4.3	3.9	5.0

per cent and in that from the second foot to 0.11 per cent, agreeing well with the results of the analysis of the samples taken the previous year. The amount of nitrogen in the surface soil is large, but smaller than that found by Shutt in surface soils from other parts of the same steppe; it is probable that the latter were sampled to a depth of only 4 or 6 inches. The percentage of potash is high and that of phosphoric acid fairly high, at all depths. The mineral constituents, with the exception of the carbonates, are uniformly distributed. In the presence of the generous supply of calcium carbonate the soil should be considered as of the first quality.

While the chemical analysis indicates this to be a fertile soil, there is nothing in the analytical results to explain the remarkable crop yields that have been obtained. There was, however, found to be something striking in the relation of the moisture content of the fields under different surface conditions. A comparison of the moisture content of the third, fourth, fifth and at times even the sixth foot of a field, that had just brought a crop of cereal or grass to maturity, with that of a field of fallow, even in a year of unusually abundant and well distributed rainfall, indicated that the moisture stored in the subsoil played a very important part in the production of the large yields. Even in the absence of any moisture determinations, the casual examination of the first 4 feet of soil of adjoining fields, that possess a similar surface soil, will show that studies of the soil to a depth of only 16 inches or even, in most places, to a depth of 3 feet are insufficient. The fourth foot of boulder clay subsoil is moist and sticky in the fallow fields while that in grass and in grain fields, when the plants have just reached maturity, resembles an ash-heap. An examination to a depth of less than 3 feet may, at times, fail to reveal any important difference between moisture conditions of grain and fallow fields. Also, examinations made long before or after the maturing of the crop may fail in the same respect. It appears probable that the soil of the whole first 5.5 feet contributes freely of plant food to the growing crops, supplying not only potassium and phosphorus, but also nitrates, under the system of cultivation employed on the Indian Head

farm. The penetration of the roots to the stored moisture, rather than the elevation of the latter, by capillarity, to the roots, is evident from the extreme dryness of the soil as deep as roots were found and the very rapid rise in the moisture content through the succeeding 6 inches, in the case of the field of rye grass, mentioned below. It is a very important matter in arid regions whether the roots penetrate the subsoil to the moisture or whether the latter is elevated to them by the slow action of capillarity. If the latter were the case, practically the only plant food furnished them from below would be nitrogen in the form of nitrates, which had been formed by the nitrification of the humus of the surface soil and had afterwards been carried by seepage below the depth of the plant roots. If the surface soil were deficient in calcium carbonate, while the subsoil was well supplied with it, this compound, also, might be elevated in solution. The chemical composition of the subsoil would then be a matter of little importance so long as the amount of calcium carbonate in the surface soil was sufficient to supply not only the lime required for plant growth and to balance the magnesium content, but also to prevent the soil becoming acid in reaction. On account of the abundance of calcium carbonate in the surface soil of the second steppe the depth to which plants of economic importance send their roots will determine to what depth the chemical composition of the soil should be studied. We should thus have to consider, in the case of the fields at Indian head, the total supply of nitrogen, potash and phosphoric acid within reach of the plant as equivalent to 0.23 per cent, 2.15 per cent and 0.77 per cent, respectively, of the surface foot, when the roots penetrate to a depth of 5 feet. The nitrogen of the soil below the first foot is not included in this total because it is not certain that nitrification occurs to any considerable depth below the first foot.¹ The distribution of plant food throughout the whole depth of soil penetrated by the roots has decided advantages over its accumulation near the surface, especially in the case of a soil that is stored with moisture and that must depend for its supply of water upon a light,

¹ Ladd : N. D. Expr. Sta. Bull. No. 47, p. 69.

uncertain rainfall. In the former case food would be furnished in a more or less regular supply from the beginning of the season of plant growth until the end, or until the moisture of the subsoil had been exhausted.

Moisture Conditions of the Surface Soil and of the Subsoil.

The samples were obtained by the writer in July, 1904, and in September, 1905, a 1.5 inch auger being used for the purpose. A large number of samples would have been desirable, but the difficulty of carrying on the investigations, when the drying of the samples had to be done at a distance of over 1,000 miles from the fields, limited the number of determinations. That the samples shipped to this laboratory were fair specimens of the various fields at the different depths was confirmed by the careful examination on the spot of the soil from similar depths in various parts of the fields. Each sample is the average of the foot section from 2 or more holes in the same field, the soil being weighed as soon as removed and placed in light cotton sacks of known weight and later dried in this laboratory at 100°. All determinations were made in duplicate.

The amount of available or "free" moisture, the total moisture less the hygroscopic moisture per acre-foot, is given in Table IV. In the calculation of the weight of water from the percentage of moisture, the writer has assumed the weight of an acre-foot of dry soil to be 3,348,000 pounds.¹ The weight of an acre-inch of water is about 113 tons.

Fields A, B and C are at Indian Head, on the experimental farm, while F and G are 1 mile south of Moose Jaw and 54 miles west of the first-mentioned fields.

Field A was seeded with Western Rye Grass, a native, in 1901, and had been cut for hay every year since, being mown on July 23, 1904, and July 13, 1905. In the latter year, between the time of haying and that at which the samples were taken, 4.26 inches of rain fell.

Field B, which adjoins A, was in fallow in 1904 and in oats in 1905. The crop was cut September 1st.

¹ Shutt: Rep. Canad. Expt. Farms, 1900, p. 157.

Field C was in fallow in 1904 and in wheat in 1905. The crop was cut on August 27th.

F and G were adjoining fields on the same farm. They were selected because they promised to give the extremes of moisture content on the type of soil of which they were representative. The latter is a very heavy, lacustral clay, uniform to a depth of more than 6 feet. F was an unusually well-tilled summer-fallow, having been in wheat in 1904, while G, which had been fallowed the previous year, bore a very heavy crop of wheat in 1905. It had been cut about September 1st.

In 1904, the last rain previous to the time of sampling was on July 17th, when 0.15 inch fell. In the following year heavy showers fell at Indian Head on August 30th and 31st., amounting to 1.28 inches of rain. At Moose Jaw, in the same year, no rain had fallen during the 10 days preceding the day on which the samples were secured.

The depth to which the chemical composition of the soil needs to be investigated is an unsettled question. That a depth of 1 foot or less is quite insufficient in the case of soils on the second steppe is evident from the above data. About 400 tons of water had been removed from the subsoil of fields B and C from depths of more than 1 foot. In the case of field G probably over 600 tons had been removed from the soil below a depth of 12 inches. These quantities of water, under the climatic conditions there prevailing, must have been removed almost entirely by the transpiration of the wheat and oat plants. According to the experiments of King¹ this weight of water would account for the growth of about 1 ton of dry matter, or approximately 15 bushels of wheat per acre. The ratio of grain to straw on field G was found to be 1.00 to 1.35, both dried at 100°. If such a large amount of water remains in contact with the particles of the deeper portions of the subsoil for nearly a year and does not pass through the surface soil on its way to the plant roots, the food supply of the plants must be largely affected by the chemical composition of the subsoil. Investigations² of the moisture content of the soil to

¹ King: "Irrigation and Drainage," p. 97 (1899).

² Shutt: Rep. of Canad. Expt. Farms, p. 157 (1900).

Table IV.

Available moisture in fallowed fields compared with that in fields that have just brought a cereal or grass crop to maturity. The water is expressed as tons per acre-foot.

Field.	Date.	First foot.	Second foot.	Third foot.	Fourth foot.	Fifth foot.	Sixth foot.	Total.
A	July 25, 1904	127	75	97	112	84	101	596
"	Sept. 4, 1905	268	157	167	177	170	152	1091
	Excess in second year	141	82	70	65	86	51	495
B	July 25, 1904	291	184	196	199	236	194	1800
"	Sept. 5, 1905	179	95	77	69	167	211	798
	Excess in fallow	112	89	119	130	69	—17	502
C	July 25, 1904	350	272	279	216	144	.	1261
"	Sept. 5, 1905	270	158	144	97	182	.	734
	Excess in fallow	80	114	135	119	—38	.	527
F	Sept. 9, 1905	162	412	360	266	236	231	1667
G	"	144	99	104	194	213	228	982
	Excess in fallow	18	313	256	72	23	3	685

a depth of 16 inches have failed to account for the good yields of grain obtained from the fallowed fields in dry seasons, while the explanation becomes evident when the investigations are carried to a depth of 6 feet. It is probable that the chemical as well as the physical properties of the subsoil play an important part in the production of cereal and grass crops on the great plains.

Ten Eyck¹ has found that the roots of wheat, oats and various grasses reach a depth of from 4 to 6 feet in North Dakota and in Kansas. Evidently the great depth of root penetration is characteristic of the whole of the great plains region.

Summary and Conclusions.

In the following there are given some conclusions of a purely agricultural nature. The detailed discussion of the data upon which they are based will be published elsewhere, in the near future.

1. The region of prairie and plain north of the northern boundary of the United States consists of 3 prairie levels or steppes.

2. The remarkably large crop yields obtained on the second steppe are confined to wheat, oats, barley, peas and potatoes.

3. These high yields have, in general, been obtained from fields that were, during the previous season, under clean cultivation, summer-fallow, or were in cultivated crops, as corn and potatoes.

4. The moisture stored in the subsoil during the previous summer and not the frost of the preceding winter, is the cause of the high yields.

5. The soil of the southern portion of the second steppe does not remain permanently frozen at any depth.

6. The surface soils are rich in nitrogen and both surface soil and subsoil are well supplied with potash and phosphoric acid. The subsoil is very rich in carbonates.

7. The roots of cereals and grasses penetrate the subsoil to

¹ Bulls. 36 and 43, N. D. Expr. Sta. ; No. 127 Kansas Expr. Sta.

depths of from 5-6 feet, even in seasons of unusually heavy and well distributed rainfall.

8. The total yield of dry matter of wheat, oats and barley varies as the rainfall of the crop season, but shows a still closer relation to the total available moisture of the crop season.

9. In the case of wheat the yield of grain from fallowed fields is largely independent of the rainfall of July and August, provided that the rainfall of May and June has been abundant.

10. Investigations of the fertility of the soils of the second steppe, in which only the first 16-36 inches are considered, do not furnish sufficient data upon which to base generalizations ; in all such investigations the composition of the soil to a depth of 5 or 6 feet should be considered.

11. The relative fertility of different areas seems to depend upon the nature of the subsoil rather than upon that of the surface soil, the latter, in general, being rich enough to produce very heavy crops when the moisture conditions are favorable.

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IONIC VELOCITY AND IONIC HYDRATION.

[FIRST COMMUNICATION.]

BY CHARLES G. CARROLL.

That there is a relation between ionic friction and the mechanical friction, or viscosity of the solvent, has long been held. To account for this relation Kohlrausch¹ proposes the following hypotheses : " About every ion moves an atmosphere of the solvent whose dimensions are determined by the individual characteristics of the ion . . . The electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere . . ." Into this form Kohlrausch puts the commonly held conception of ionic hydration or combination of ion and solvent. Numerous attempts have been made to measure the amount of such hydration, and an

¹ P. Roy. Soc., 71, 338.

actual transport of solvent with the ions has been demonstrated by Morgan and Kanolt¹ and by Buchböck.²

The evidence for the Kohlrausch hypothesis was, however, incomplete and no attempt was made to put it on a quantitative basis. A quantitative application was made by the writer,³ in the case of certain ions and salts, in methyl and ethyl alcohols as solvents. It was shown that, for a considerable range of temperature, the maximum molecular conductivity of any given salt varies inversely as the coefficient of viscosity, or,

$$\mu \propto \eta = \text{constant.}$$

In every case considered, embracing all the data available at the time, good agreement between fact and theory was found, and recently Walden⁴ has shown that the foregoing relationship holds for tetraethylammonium iodide in some 20 organic solvents.

No general law has been found to hold for ionic velocities, or conductivities, in aqueous solution. The purpose of the present paper is to show that a general law relating to ionic velocity, or conductivity, viscosity and other properties of solvent and solute exists for solutions in water and methyl alcohol. This law may be stated as follows :

The velocity of a given ion, under a constant fall of potential, is directly proportional to the valence of the ion, the cube root of the ionic (atomic) volume, the specific inductive capacity, or dielectric constant, of the solvent, and is inversely proportional to the viscosity coefficient of the solvent.

Formulated, the law is, for cations,

$$\frac{c \eta}{n_1 D \cdot V_c^{1/3}} = K_c ;$$

for anions,

$$\frac{a \eta}{n_2 D \cdot V_a^{1/3}} = K_a,$$

¹ THIS JOURNAL, 28, 572.

² Z. physik. Chem., 45, 563.

³ Dissertation, Johns Hopkins University, 1904. Jones and Carroll: THIS JOURNAL, 32, 521.

⁴ Z. physik. Chem., 55, 207.

where c and a are the velocities of cation and anion, respectively, n_1 and n_2 their valences, η is the viscosity coefficient; D , the dielectric constant of the solvent; and $V_c^{1/3}$ and $V_a^{1/3}$ are the cube roots of the atomic volumes of the elements yielding the ions. It is assumed that, for the same element, ionic and atomic volume are equal. Accordingly, if the ions be spherical in shape, the cube roots of the various atomic volumes will be proportional to the various atomic, or ionic, radii.

The law may be tested by the use of relative ionic velocities, or by the use of conductivity data, if the values of the constants K_c and K_a have been determined, for we have

$$\frac{(c + a)\eta}{D\left(n_1 V_c^{1/3} + \frac{K_a}{K_c} n_2 V_a^{1/3}\right)} = \text{constant.}$$

In this case n_1 and n_2 are the number of unit changes carried by cation or anion, or cations or anions, collectively.

In the following table are given the results of a comparison for certain ions in aqueous and methyl alcoholic solution.

Table I.—Values of K_c and K_a for Various Ions.

$\eta_{\text{H}_2\text{O}} - 18^\circ = 0.01054.^1$		$\eta_{\text{CH}_3\text{OH}} - 25^\circ = 0.00553.^1$			
$D_{\text{H}_2\text{O}} - 18^\circ = 80.8.^2$		$D_{\text{CH}_3\text{OH}} - 25^\circ = 31.7.^2$			
Ion.	Ionic volume ³	Velocity, H_2O^4	Velocity, CH_3OH^5	$K_{c,a} \times 10^6$, H_2O .	$K_{c,a} \times 10^6$, CH_3OH .
Li	11.9	33.4	27.8	191	212
Na	23.7	43.6	37.3	198	227
K	45.5	64.7	45.9	236	224
Rb	56.3	68.0		231	
Cs	70.6	68.0		215	
Ca	25.3	51.8		230	
Sr	34.5	51.7		207	
Ba	36.5	55.5		218	
Cl	25.4	65.4	49.5	290	294
Br	25.6	67.6	50.2	299	297
I	25.6	66.4	52.4	293	310

¹ Thorpe and Rodger: Phil. Trans., 185A, 397.

² Drude: Wied. Ann., 59, 49.

³ Ostwald: "Lehrbuch," I., 854.

⁴ Kohlrausch: Sitzun. d. k. p. akad., 26, 572.

⁵ Carrara: Gazz. chim. ital., 26, 179.

The mean value of K_c is 220, of K_a 297. The ratio K_a/K_c equals 1.35. With certain exceptions the values for the constants agree tolerably well, particularly in the case of the ions in methyl alcohol.

It remains to test the law by means of conductivity data. This is done in the following tables :

Table II.—Values of K for Various Salts in Aqueous Solution.

	$K \times 10^5$				
	Cl.	Br.	I.	NO ₃ .	SO ₄ .
Li	208			200	
Na	209	219	216	201	204
K	226	230	228	215	224
Rb	222				
Cs	216				
Ca	219			205	218
Sr	217			202	
Ba	216			191	
Zn	236				229
Mg	226				205
Tl	237	237		224	
Cd	220				213

For RbCl, CaCl₂, BaCl₂, SrCl₂, ZnCl₂ and MgCl₂ the value of $\mu_{10,000}$ was used, for TlCl μ_{2048} , and for CdCl₂ μ_{2000} . In the other cases μ_{∞} was used. The values for certain nitrates and sulphates are given. These were calculated, using Kopp's¹ values for the volumes of the NO₃ and SO₄ groups. The conductivity data were taken from Landolt and Börnstein's "Tabellen," ed. 1905. The values for the constants, D , η , etc., are from the same sources as in Table I.

Table III.—Values of K for Various Salts in Methyl Alcohol Solutions.

		$K \times 10^6$.
NaCl	25°	227
NaBr	25°	233
NaI	18°	230
KCl	25°	227
KBr	25°	229
KI	18°	217

¹ Ostwald: "Lehrbuch," I., 845.

The values for μ_{∞} at 25° were taken from the results of Carrara;¹ those at 18° from Völlmer.² Values of other constants were obtained from sources already indicated.

Finally, it can be shown that the foregoing law is susceptible of a simple physical explanation.

Assuming the ion to be spherical in shape and that the charge carried is uniformly distributed over its surface, as is the case with a charged spherical conductor, the capacity of the ion, considered as a spherical condenser, will be found from the relation,

$$(1) \quad \pi = e/c,$$

where π = potential, e = quantity and c = capacity. The capacity of a sphere varies directly as its radius;

$$c = K \cdot V, \text{ or, for the ion}$$

$$c = K \cdot V^{1/3} \text{ and}$$

$$(2) \quad \pi = K \cdot e/V^{1/3}.$$

Now, if a charged body is brought into the presence of particles of substance free to move, these, if of greater specific inductive capacity than the surrounding medium, will be attracted to the charged body, thus running down the energy of the field around the charged body. It is reasonable to suppose that in different cases the amount of such lowering of energy is equal. Applying these considerations to the ions, the thickness of the shell of solvent formed at any point by attraction, will be determined by the potential at that point and by the specific inductive capacity of the solvent,

$$(3) \quad r_s = K \cdot \frac{\pi}{D} = K \cdot \frac{1}{D \cdot V^{1/3}},$$

since
$$\pi = K \cdot \frac{1}{V^{1/3}}.$$

According to Stokes, when a sphere moves with a small velocity in a viscous fluid, the frictional resistance is proportional to the product $\eta r V$, V being the velocity, r the radius of the sphere and η the viscosity coefficient, and the limiting

¹ *Loc. cit.*

² *Wied. Ann.*, 52, 328.

velocity of the sphere, when the force acting is uniform, is inversely proportional to the product $r \eta$.

Applying this to the ion and its shell of solvent and taking the thickness of the shell, r_s , as equal to the effective ionic radius, or actual ionic radius plus shell thickness, we have, for ionic velocity,

$$(4) \quad V = K. \frac{I}{\eta r_s},$$

and substituting for r_s its value from (3), we get

$$(5) \quad V = K. \frac{D V^{1/3}}{\eta},$$

which is a different form of the original equation formulating the law.

In the foregoing derivation it is assumed that the thickness of the shell of solvent, r_s , is so great as compared with the real ionic radius, $K. V^{1/3}$, that r_s may be put for $r_s + K. V^{1/3}$ without much error. It is evident that for ions of large ionic volume r_s and $K. V^{1/3}$ must be more nearly equal than for ions of small ionic (atomic) volume. The complete expression would be

$$V = K_1 \frac{I}{\eta \left(K_2 V^{1/3} + K_3 \cdot \frac{I}{D \cdot V^{1/3}} \right)}.$$

If $K_2 V^{1/3}$ is small as compared with $K_3 \cdot \frac{I}{D \cdot V^{1/3}}$, we get equation (5). Here, then, we have a possible explanation of some of the discrepancies in Table I.

Summary.

1. The hypothesis of ionic hydration has been shown to be capable of a quantitative application in the form of a general conductivity law.

2. This law has been shown to have a simple physical explanation.

1,3,5-TRIOD-2-CHLORBENZENE.

By W. V. GREEN.

Much work has been done in this laboratory on the replacement by hydrogen of bromine or iodine attached to the benzene ring, under the influence of sodic ethylate, sodic malonic ester, or sodic acetacetic ester. In most cases the halogen replaced by hydrogen has stood in the diortho position to 2 nitro groups, but it has been found also¹ that this reaction takes place, when the atom of halogen is in the diortho position to 2 atoms of bromine or chlorine. The work described in this paper was undertaken with the intention of studying the effect of 2 atoms of iodine on an atom of halogen standing between them, but unexpected obstacles have delayed it so much that only one preliminary experiment of this sort could be tried; nevertheless, as I shall be unable to continue the work in this laboratory next year, it seems best to publish this description of the results obtained.

The 1,3,5-triiod-2-chlorbenzene was made by replacing with chlorine the amino group in symmetrical triiodaniline, but if the triiodaniline was not carefully purified, another substance was formed, which it was found impossible to separate from the desired product. The triiodchlorbenzene melts at 119°-120°, and, when boiled for 6 hours with an alcoholic solution of sodic ethylate, gave up iodine, although the reaction was far from complete. Only a single experiment was tried with a small amount of material, so that more work is necessary to understand the nature of the reaction, but there seems no doubt that this compound behaves differently from the corresponding tribromchlorbenzene, which is unaffected by sodic ethylate under these conditions. The subject, therefore, deserves further study, which will be given to it in this laboratory.

When treated with cold, fuming nitric acid the triiodchlorbenzene is converted into triiodchlor-dinitrobenzene, which de-

¹ Jackson and Calvert: *THIS JOURNAL*, 18, 298. Jackson and Gazzolo: *Ibid.*, 22, 50.

composes and melts from 266° – 269° . This seems to be a very reactive substance, as preliminary experiments showed that it acted with aniline, sodic ethylate, sodic malonic ester, or sodic acetacetic ester. These reactions will also be studied in this laboratory.

Preparation of 1,3,5-triiod-2-chlorbenzene, $C_6H_2I_3Cl$.—The triiodaniline was prepared by a process founded on those of Michael and Norton¹ and of Jackson and Langmaid,² as follows: Ten grams of freshly distilled aniline, dissolved in 500 cc. of strong hydrochloric acid and diluted up to 7 liters, were treated with 54 grams of the monochloride of iodine, ICl , introduced by passing a stream of air through the flask containing the chloride, which was heated to 60° . The introduction of the chloride took from 90–110 minutes. The brown precipitate formed at first and the straw-yellow one deposited later, are both triiodaniline, and the yield of this crude product in the most favorable cases ran as high as 90 per cent of the theory. The triiodaniline thus obtained was recrystallized from chloroform until it showed the melting point 184° – 185° . If the crude product was used in making the triiodchlorbenzene, a substance melting at 166° was also formed, which it was almost impossible to separate from the desired product. This impurity seemed to be due to the use of an excess of chloride of iodine in making the triiodaniline; and, as in this case, vapors of iodine were given off during the diazo reaction, giving $C_6H_2I_3Cl$, it is possible that these phenomena may be due to the introduction of iodine into the amino group. The filtrate from the triiodaniline should not be used for dissolving a fresh portion of aniline for a second operation, as this gave a much less pure product than when fresh hydrochloric acid was used.

The triiodaniline was converted into triiodchlorbenzene as follows: Ten grams of the triiodaniline were treated with 120 cc. of strong hydrochloric acid and 15–20 grams of very finely powdered sodic nitrite added to it in small portions at a time; after each addition the mixture was shaken in a loosely corked

¹ Ber. d. chem. Ges., **21**, 1707 (1888).

² THIS JOURNAL, **32**, 300 (1904).

flask, until all red fumes had been absorbed. The decomposition of the diazo compound was then brought about by heat and the flask allowed to stand on the steam-bath for 2 hours after the evolution of nitrogen had slackened. The product was purified by washing with sodic hydrate and water, followed by crystallization from a mixture of benzene and alcohol, until it showed the constant melting point 119° – 120° , when it was dried at 100° for analysis. If the product was very tarry, it was found advisable to wash it with ligroin and later with small quantities of ether and with alcohol, before crystallizing. Treatment with bone-black absorbed much of the substance and sublimation gave unsatisfactory results. The yield varied from 80 to 85 per cent of the theory.

I. 0.1926 gram substance gave 0.3312 gram AgI + AgCl.

II. 0.1402 gram substance gave 0.2413 gram AgI + AgCl.

	Calculated for $C_6H_2I_3Cl$.	I.	Found. II.
I + Cl	84.92	84.37	84.47

Properties of Triiodchlorbenzene (1,3,5,2).—When crystallized from a mixture of benzene and alcohol it forms slender prisms, terminated by pyramids, which are probably white, but could not be obtained free from a faint pinkish tinge. These appear, when seen with the naked eye, as thick masses of branching needles. It melts at 119° – 120° , and is freely soluble in ether, chloroform, acetone, benzene, toluene, carbonic disulphide, or ethyl acetate; somewhat soluble in glacial acetic acid or acetic anhydride; very slightly soluble in cold alcohol, or methyl alcohol, more soluble in them when hot; essentially insoluble in ligroin, water, or cold amyl alcohol, moderately soluble in hot amyl alcohol. Aniline dissolves it freely, forming a red solution, but no halogen is removed. The best solvent for it is a mixture of benzene and alcohol. It does not seem to be affected by the 3 strong mineral acids, or sodic hydrate, but fuming nitric acid acts upon it in a way described later in this paper.

A preliminary experiment was tried on the action of sodic ethylate with the 1,3,5-triiod-2-chlorbenzene. The alcoholic solution used contained more than enough ethylate to remove

all the halogen and it was mixed with enough anhydrous benzene to insure the solution of the triiodchlorbenzene. The mixture, which took on a pinkish color at once, was heated on the steam-bath, under a return condenser, for 6 hours, when it passed through red to brownish-red. It was poured into a quantity of water, which formed a viscous, red precipitate and yellow, turbid liquid, and the mixture was allowed to stand for 2 days to get rid of the benzene before it was filtered. Unfortunately, the amount of material available for this experiment, a little over 0.8 gram, was so small that no investigation was possible of the red organic product, which had a characteristic smell like apples. The still turbid, aqueous filtrate was acidified with nitric acid and filtered again from a slight precipitate; on acidification the color of the liquid changed from yellow to red, probably from the formation of some free iodine, which was detected by starch paste and by carbonic disulphide. This filtrate, which became colorless on standing over night in a stoppered flask, was made up to 1 liter, and 2 measured portions were treated with argentic nitrate, which gave a yellowish-white precipitate. There can be no doubt from these results that sodic iodide was one of the products of the reaction, but the amount of AgI obtained was less than 30 per cent of that which would have been formed, if 1 atom of iodine had been removed. It is evident, therefore, that the reaction was far from complete. This replacement of iodine shows that the behavior of the triiodchlorbenzene with sodic ethylate is different from that of the corresponding tribromchlorbenzene, which is unaffected by sodic ethylate under these conditions. An attempt was next made to determine whether this precipitate contained AgCl as well as AgI. With this intention it was washed with ammoniac hydrate, which removed only about the amount of silver salt corresponding to the solubility of AgI in ammoniac hydrate; it is probable, therefore, that no AgCl was present, but further experiments are necessary to decide the question.

1,3,5-Triiod-2-chlor-dinitrobenzene, $C_6I_3Cl(NO_2)_2$.—The triiodchlorbenzene was dissolved in cold, fuming nitric acid, when, after standing for a short time, long needles of the

dinitro compound separated. The mixture was then diluted with water, warmed on the steam-bath, filtered and washed. The filtrate gave no test for a halogen. The organic product was recrystallized from a mixture of benzene and ligroin until it showed the decomposition point 266° – 269° , when it was dried, at 120° , for analysis.

I. 0.1306 gram substance gave 0.1901 gram $\text{AgI} + \text{AgCl}$.

II. 0.1341 gram substance gave 0.1949 gram $\text{AgI} + \text{AgCl}$.

	Calculated for $\text{C}_6\text{I}_3\text{Cl}(\text{NO}_2)_2$.	I.	Found. II.
I + Cl	71.74	71.47	71.34

Properties of 1,3,5-Triiod-2-chlordinitrobenzene.—It crystallizes from a mixture of benzene and ligroin in yellowish-white needles, which, under the microscope, are seen to be prisms terminated by pyramids, or occasionally by a plane at right angles to the axis, which seem to belong to the orthorhombic system. At 266° it turns black, and begins to melt at 267° , but the fusion is not complete until the temperature reaches 269° . It is freely soluble in ether, chloroform, acetone, benzene, toluene, carbonic disulphide, or ethyl acetate; somewhat soluble in glacial acetic acid or acetic anhydride; nearly insoluble in cold methyl, ethyl, or isoamyl alcohol, moderately soluble in these solvents when hot; essentially insoluble in water or ligroin. The best solvent for it is a mixture of benzene and ligroin. The 3 strong mineral acids seem to have no action on it. Sodid hydrate seems to react with it, as a slight precipitate was formed by argentic nitrate in the acidified solution.

The triiodchlordinitrobenzene is a decidedly reactive substance. Aniline forms with it a red solution with the removal of some halogen, when heated on the steam-bath. Sodid malonic ester gives with it a strong red color, sodid acetacetic ester a yellow, sodid ethylate a light red color. In each case a precipitate was formed, when argentic nitrate was added to the acidified solution.

The research will be continued in this laboratory.

CAMBRIDGE, MASS.,
July 9, 1906.

THE NITRATION OF ANILINE AND CERTAIN OF ITS DERIVATIVES. I.

BY J. BISHOP TINGLE AND F. C. BLANCK.

It is well known that aniline cannot be directly nitrated; under any of the ordinary conditions in which such action might be expected to take place, nitric acid converts aniline into a resinous, tarry, or charred mass. This behavior is usually accounted for by stating that the nitric acid attacks the amino group more readily than the benzene nucleus.¹ A little thought will show that such a statement, although it *may* be true, is really devoid of any experimental foundation and that certain rather serious objections could be urged against it. For instance, it has been suggested by some chemists that substitution in the nucleus is really preceded by substitution in the side chain and subsequent rearrangement. Further, the amino group is even more sensitive towards nitrous acid than towards nitric acid, as is shown by the fact that, in general, nitrites of the aromatic amines cannot be prepared, whereas the nitrates are usually stable; moreover, in carrying out the diazo reaction, some tarry matter is always formed and unless considerable care is taken to adjust the conditions of the experiment specially for each individual amine, this tar is apt to be the chief, or even the only tangible product of the reaction.

Guided by these considerations, we decided to reinvestigate the direct nitration of aniline and to begin a systematic survey of the influence, on nitration, of the substitution in aniline of one or both of the hydrogen atoms of the amino group. Coupled with this, however, is the further question of the influence exercised on the substitution by admixture of the nitric acid with other acids. These points are illustrated by the fact that dimethylaniline yields the paranitro derivative when nitrated in the presence of acetic acid,² whereas the meta compound is formed if sulphuric and nitric acids be used.³ A number of cases are on

¹ *Vide*, for example, Lassar-Cohn's "Application of Some General Organic Reactions," translated by J. Bishop Tingle, p. 3, *et seq.*

² Ber. d. chem. Ges., 10, 761.

³ *Ibid.*, 19, 198.

record where mixtures of nitric and acetic acids or nitric and sulphuric acids have been employed to nitrate some compound, but this is the only example which we have been able to find in the literature of nitration experiments having been made on a given aniline derivative with each of these mixtures of acids. The influence of the substituting group is shown by the fact that formanilide, for example, yields the paranitro derivative by direct nitration,¹ whereas, under the same conditions, acetanilide gives rise to a mixture of ortho and paranitro compounds.²

The investigation just outlined will, naturally, extend over a considerable time and we wish to reserve the field by the publication of this paper, which, although it is of a preliminary nature, contains results that we think may prove to be of some general interest.

Nitration of Aniline.—Our experiments in this connection being based upon the hypothesis that nitrous acid might probably be the active agent in producing the decomposition of the aniline, we took every precaution in our power to exclude this substance and to remove it if it were formed. Accordingly, the nitric acid which was used was freed from dissolved oxides by means of a current of dry air and, as far as possible, oxidation during the experiment was avoided by employing nitric acid of 99 per cent concentration and freshly distilled aniline. We carried out the experiments in platinum vessels, placed in a freezing mixture, so as to keep the temperature as low as possible, and took care that the reagents were gradually mixed and thoroughly stirred; moreover, we operated in the presence of urea, in the hope that any nitrous acid which might be produced by the possible reduction of some of the nitric acid would be instantly decomposed by this reagent. In the later experiments we employed aniline nitrate in place of aniline, so as to eliminate the heat of formation of this salt. In every experiment, however, it was found to be impossible to keep the temperature sufficiently low and, as soon as it rose, tarry, or carbonaceous products were formed. The

¹ THIS JOURNAL, 8, 346.

² "Jahresb.," 1875, p. 344. THIS JOURNAL, 11, 320.

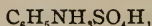
result was identical whether the acid was added to the aniline or *vice versa*.

These experiments were, therefore, discontinued and another series undertaken in order to determine at what concentration of nitric acid the formation of aniline nitrate ceases and nitration—or charring—begins. The results demonstrated that any strength of acid could be used up to at least 75.33 per cent HNO_3 , provided, in the case of the more concentrated acids, above 50 per cent, that the mixture was cooled and excess of acid was avoided. Acids of 50.71–75.33 per cent always gave, with aniline, a pink-colored solid, which was stable at 0° ; the color was at once discharged by the addition of a little water, or of a few drops of aniline. Slight excess of acid increased or restored the color, as the case might be, but if this additional acid was of sufficient concentration then, sooner or later, depending on this concentration and on the temperature, the pink color darkened, finally becoming black and the whole mass gradually charred, sometimes becoming incandescent. We have been unable to find any previous record of these phenomena.

With acid above 75.33 per cent HNO_3 , charring took place rather quickly although the aniline was in considerable excess. We believe, however, that this was due to the impossibility of preventing local superheating, *i. e.*, to the action of the concentrated acid, at a relatively high temperature, on aniline nitrate. Be this as it may, it is certain that with acids containing up to 75.33 per cent HNO_3 , any charring which may be brought about is due to an attack on aniline nitrate and not to one on free aniline. We emphasize this rather obvious fact in order to contrast it with the behavior of aniline towards a mixture of nitric and sulphuric acids, in which the latter is in considerable excess. In these circumstances, as is well known, nitration proceeds smoothly, because, as it is usually expressed, the sulphuric acid “protects” the amino group. Surely, however, the amino group is equally well “protected” in the nitrate,



as in the sulphate,



and the excess of concentrated sulphuric acid which is present must abstract so much water from the nitric acid as to make it of a higher concentration than 75.33 per cent HNO_3 . The only very obvious difference in the conditions of the 2 experiments, so far as we can see, is in that which governs the temperature. In the experiment with sulphuric acid all the materials are in solution and the "heat of nitration," as it may be termed, is instantaneously absorbed and diffused throughout the large volume of comparatively indifferent sulphuric acid, whereas, in our experiments with aniline nitrate and nitric acid, we had to rely on the relatively slow, inefficient and clumsy mechanical means of stirring and external cooling to neutralize this heat. We hope, later, to recur to this point, when more experimental data have been accumulated.

Nitration of Anilines Substituted in the Amino Group.—A considerable amount of scattered work, which will be cited in due course, has been done on the nitration of compounds of the types $\text{C}_6\text{H}_5\text{NHR}$, $\text{C}_6\text{H}_5\text{NRR}'$ and $\text{C}_6\text{H}_5\text{N}:\text{R}''$, and in some of these experiments the nitric acid was mixed with sulphuric or acetic acids. This portion of our investigation has been carried out with the following reagents: 1. Nitric acid, sp. gr. = 1.46,¹ containing 80 per cent HNO_3 ; 2. Nitric acid, sp. gr. 1.46, with glacial acetic acid, usually in the proportion 1.25 mols. of nitric acid : 4 mols. of acetic acid, or 1.25 mols. of nitric acid : 8 mols. of acetic acid; 3. Nitric acid, sp. gr. = 1.46, and anhydrous oxalic acid, in the proportion 1.25 mols. of nitric acid : 4 mols. of oxalic acid; 4. Nitric acid, sp. = 1.46, and trichloroacetic acid, in the proportion 1.25 mols. of nitric acid : 4 mols. of trichloroacetic acid; 5. Nitric acid, sp. gr. = 1.46, and concentrated sulphuric acid, sp. gr. = 1.83, containing about 92 per cent H_2SO_4 , in the proportion of 1.25 mols. nitric acid : 4 mols. of sulphuric acid. The dissociation constants of these admixed acids are as follows: Acetic acid, $K = 0.0018$; oxalic acid, $K = 10.00$; trichloroacetic acid, $K = 121.00$; sulphuric acid, $K = 130.0$, approximately, by calculation. It will be observed that we have selected, for admixture with the

¹ Remsen and Graham: *THIS JOURNAL*, 11, 320.

nitric acid, acids of widely differing strength. Acetic is a typical "weak" acid; trichloroacetic is, practically, the strongest organic acid which is known and certainly the strongest which is available for use in any quantity. Oxalic acid was selected partly because it is dibasic, but chiefly because of its intermediate position between the other two. The use of sulphuric acid was dictated by the fact that it is the only "strong" inorganic acid suited for the purpose in view. It will be noticed that, in so far as "strength" is concerned, sulphuric and trichloroacetic acids are in the same class¹ and should, therefore, permit of a conclusion being drawn as to the influence, if any, of the mono or dibasicity of the admixed acid and of its organic or inorganic composition, *i. e.*, as to the possible specific influence of a carboxyl group.

As far as possible, we desired to avoid the formation of di- or polynitro derivatives, consequently, our experiments were usually carried out at room temperature; in cases where there was a considerable evolution of heat on mixing the substances, cooling with ice-water was resorted to. Sometimes the mixtures were surrounded by crushed ice during the whole time of an experiment and occasionally gentle warming was requisite to promote a reaction.

Formanilide.—This substance yields paranitroformanilide by direct nitration.² In the presence of sulphuric acid we have obtained the *meta* derivative.

Acetanilide.—This compound, by direct nitration, gives a mixture of ortho and para derivatives.³ In the presence of acetic acid no nitration took place under the conditions of our experiments. With oxalic acid we obtained *paranitroacetanilide* in good yield. The same result was produced by the use of trichloroacetic acid, which was ground up with the acetanilide and the mixture added to the nitric acid. Sulphuric acid yielded *metanitroacetanilide*. This last result differs from the experience of Nölting and Collin,⁴ who, however, operated in a freezing mixture of ice and salt and, nitrating in the presence of

¹ Cf. Kastle: *THIS JOURNAL*, 33, 52 (1905).

² *Ibid.*, 8, 346.

³ "Jahres," 1875, p. 344. *THIS JOURNAL*, 11, 320.

⁴ *Ber. d. chem. Ges.*, 17, 261.

both acetic and sulphuric acids, obtained the para and ortho derivatives.

Benzoylanilide.—A mixture of ortho, meta and paranitro derivatives is formed by the direct nitration of this compound.¹ Operating in the presence of sulphuric acid we have only found the *para* compound.

By the use of acetic acid we have obtained the *meta* isomer, practically without admixture.

Methylaniline.—Our experiments with this substance, in the presence of acetic acid, failed to yield any positive result. Sulphuric acid causes the production of the metanitro derivative.²

Ethylaniline.—This body behaved, with acetic acid, like the methyl compound. In the presence of sulphuric acid meta and para derivatives are formed.³

Dimethylaniline.—For the sake of completeness we include this substance, although we have no results of our own to communicate at present. Acetic acid is stated to produce the paranitro derivative,⁴ whereas sulphuric acid gives rise to the meta compound.⁵

Diethylaniline.—In our experiments with this substance, in the presence of acetic acid, nitration failed to take place. Sulphuric acid has been found to produce chiefly the meta derivative, together with some para compound.⁶

We think that our results justify the statement that *the position assumed by the entrant nitro group is definitely influenced both by the acid present with the nitric acid and also by the N-substituents*.

We hope to give full details of our experiments later, when the work on the subject, which is now in progress in this laboratory, is more nearly complete.

JOHNS HOPKINS UNIVERSITY,
June, 1906.

¹ Ann. Chem. (Liebig), 208, 292.

² Centrabl., 1901, I., p. 105.

³ Ber. d. chem. Ges., 19, 546.

⁴ *Ibid.*, 10, 761.

⁵ *Ibid.*, 19, 198.

⁶ *Ibid.*, 19, 199.

ON A NEW METHOD FOR THE PREPARATION OF STANDARD SOLUTIONS.

BY S. F. ACREE AND R. F. BRUNEL.

At the time of the publication of some work which appeared with the above title¹ the writers had overlooked the work of G. T. Moody² on the use of this method for the preparation of standard solutions of hydrochloric acid. The work is being continued as announced.

JOHNS HOPKINS UNIVERSITY,
Nov. 1, 1906.

OBITUARY.

FEDOR F. BEILSTEIN.

Professor F. F. Beilstein was born in St. Petersburg, February 5, 1838, and died in the same city, October 19, 1906. His chemical education was received from Bunsen, at Heidelberg, and¹ from Liebig, at Munich, and he obtained the Ph.D. degree from the University of Göttingen. In 1859, Beilstein was appointed assistant professor of chemistry at the University of Breslau, and in 1866 was called to the chair of chemistry at the St. Petersburg Technological Institute; this appointment he retained until his death. Beilstein's investigations were numerous and some of them had important technological results. They dealt chiefly with compounds of the aromatic series, with the composition of Caucasian naphtha and coal-tar and with analytical methods. His first paper, on the diffusion of liquids, appeared in his eighteenth year.

Professor Beilstein was the author of numerous books, all issued in the German language. By far the most important of these was, of course, his "Handbuch der organischen Chemie" by the publication of which he placed his fellow organic chemists under an immense debt of gratitude. It would, indeed, be difficult to overestimate the enormous influence, direct and indirect, exerted on the progress of organic chemical investigation by this work. Three editions of the "Handbuch" were prepared by Beilstein himself. Later, he transferred his rights to the German Chemical Society which has issued the supplementary volumes. Beilstein was elected a member of the St.

¹ THIS JOURNAL, 36, 117.

² J. Chem. Soc., 73, 658.

Petersburg Academy of Sciences in 1886, an "Honorary Member" of the German Chemical Society in 1894, and a "Foreign Member" of the London Chemical Society in 1883.

REPORT.

The Interaction of Chlorine and Hydrogen.

In a recent article¹ C. H. Burgess and D. L. Chapman describe the results obtained from a number of experiments carried out to determine the cause of the so-called "induction period," or period of comparative inactivity in the initial union of chlorine and hydrogen. The hypotheses advanced by numerous investigators of this phenomena can be grouped under one of three heads:

(a) The action is due to the power which light has of increasing the electro-negative properties of chlorine.

(b) The cause of the resistance to the action is in some manner removed by the action of light.

(c) The action is due to the formation and interaction of intermediate products. All theories were studied and found to afford unsatisfactory explanations of the phenomena.

Van't Hoff has suggested that as an induction period is not characteristic of a simple chemical reaction, the phenomena in question was due to the omission of some necessary experimental precaution. Experiments to test this point soon showed that the action is due to the presence of impurities which would produce the results noticed and would account for many of the observed facts. The mixture of chlorine and hydrogen employed was obtained by the electrolysis of a strong aqueous solution of hydrogen chloride. The actinometer in which the experiments were carried out was placed in a tank of water to keep the temperature constant.

When the apparatus is filled with the electrolytic gas and ordinary tap water and exposed to light there is no effect for some time; finally, however, the action begins and gradually increases in speed to a maximum, then falls slightly and eventually becomes constant. After this stage has been reached the gases can again be rendered inactive by shaking the vessel in which they are contained. This can be repeated a number of times, the induction period, however, becoming shorter each time. Even when the greatest precautions are taken to render the gas active, the inactivity is restored by allowing the gas to stand in the dark. If the chlorine is separately rendered active

¹ J. Chem. Soc., 89, 1399 (1906).

see W. R. V. 372681

it has no more effect upon the result than if the action takes place in the presence of the hydrogen. The facts all seemed to point to the conclusion that there was some principle which caused a resistance to combustion and which could be destroyed by light. It was present in ordinary water and freshly prepared chlorine, but not in hydrogen. At first it was thought that the restoration of this property when the gases were allowed to stand in the dark, would shut out all possibility of the action being due to any material substances.

Solutions of salts and acids were found to have a more marked influence upon the induction period than water alone; but this action can be decreased or prevented by keeping the vessel at the boiling-point of water for some time. It was found possible to prepare crystals of barium chloride, which had lost the property of destroying or removing the activity of electrolytic gas; such material is termed "active;" when these crystals were left for some time between folds of filter paper they became "inactive." It was also found that active solutions could be prepared, some of which contained no free chlorine and others were produced entirely without the agency of this element; the presence of oxygen had no influence on the action.

The evidence pointed to the fact that the substance which produced the induction period was present in the mixture used, or was extracted from the air.

Small amounts of ammonia were found to cause the induction period and to form with chlorine a product which is volatile at ordinary temperatures and can be removed from solution by exhaustion.

In these particulars there was an agreement between the results observed in the ordinary manner and those produced artificially, by the addition of the substances in question. If the impurities are completely removed and all outside contamination is prevented, there is no decay of the activity. When small quantities of ammonia were added, the induction period was roughly proportional to its amount. Other substances such as alcohol, ether, sulphur dioxide, hydrogen sulphide, nitrous or nitric acids, stannous chloride, hydrogen peroxide, potassium permanganate, etc., caused no decrease of activity. That the inactivity was restored when the gas, in which all the ammonia had been destroyed, was allowed to stand, was shown by the authors to be due to the formation of ammonia from more complex compounds. Egg albumen showed a very marked effect of this kind. The formation of condensation nuclei by the action of light on moist chlorine was also studied, but satisfactory evidence of their production from this action

was not secured. A number of authorities have claimed that a definite proportion of the rays absorbed during chemical change are expended in bringing about the change. If this is true a mixture of air and chlorine should absorb less light than a mixture of hydrogen and chlorine; but the present investigators found the extinction coefficient to be almost the same whether hydrogen and chlorine or oxygen and chlorine were the mixtures used.

Although the cause of the induction period has been discovered, the authors are unable to suggest any explanation of the phenomena without introducing suppositions for which no experimental results have hitherto been presented. J. E. G.

REVIEWS.

THE ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York: D. Van Nostrand Co. 1906. pp. viii + 212. Price, \$2.00.

The progress of physics during the decade following the discovery of radioactivity has brought forth a great number of significant facts, and a brilliant theory which not only accounts in a reasonably satisfactory manner for these facts, but also bids fair to modify profoundly the fundamental ideas of several sciences besides physics,—certainly chemistry, and very possibly mineralogy, geology and astronomy. There are thus many persons who, while lacking the time for a detailed study of these subjects, feel the need of more accurate knowledge than can be obtained from popular accounts of the wonders of radium.

It is to fill this need that Professor Jones' book is designed; those who, from an acquaintance with his previous books, are familiar with his marked ability in exposition, will not need to be told that this design has been most successfully carried out. The style is simple and non-technical, yet scientific accuracy is seldom sacrificed to simplicity of statement. To give a proper idea of the subject, the author has found it necessary to include many related topics, such as the ionization of gases, the nature of the cathode rays and the Röntgen rays, J. J. Thomson's model atoms, etc.; and, notwithstanding the brevity to which he has restricted himself, he has been able, by skilful arrangement and careful attention to perspective, to give an account of these subjects which is adequate for the purpose in hand.

When one considers the difficulties which the author of such a book has to overcome, it is not surprising that some of his

statements leave room for difference of opinion. Thus, it is probable that few physicists would agree with the implication, on pp. 22 and 23, that the hypothesis of the electrical nature of mass has any connection, even a remote one, with Ostwald's dynamically unsophisticated view that energy is the only reality and matter a mere hypothesis. Again, on p. 58, Runge and Precht's calculation of the atomic weight of radium, 257.8, is defended, as against Mme. Curie's determination, 225, by the argument that, as radium is more active than uranium, we should expect its atomic weight to be greater. Such a simple connection between atomic weight and activity is not suggested by any theory of the structure of the atom, nor is it consistent with the known relations among successive radioactive products. Thus radium emanation is, weight for weight, enormously more active than radium, radium A is more active than the emanation, radium C is less active than radium A, but more active than the emanation, while radium F (polonium) is much less active than even the emanation. If we assumed that the atomic weight followed the activity, we should have here a bewildering series of additions to, and subtractions from, the atom which it would be difficult to reconcile with any reasonable view of the process of radioactive change.

The few points, however, upon which the reader may be disposed to differ from the author will play a small part in his final estimate of the book; he can feel only admiration at the very successful solution of what must have been a difficult problem in the exposition of a new and somewhat complicated subject.

H. A. BUMSTEAD.

LES INDUSTRIES DE LA CONSERVATION DES ALIMENTS. By X. ROCQUES. Illustrated. Paris: Imprimerie Gauthier-Villars. 1906. pp. 506. Price, 15 Fr.

This is one of the volumes of the Library of Technology, prepared by M. Rocques, Director of the Laboratory of the General Warehouses of Paris, expert chemist of the Tribunals of the Seine and formerly chief chemist of the Municipal Laboratory of Paris. The introduction was written by M. Brouardel, of the Institute of Technology. The work begins with an historical sketch of the methods of preservation, and gives due credit to the discoveries of Appert, who was really the first to succeed in preserving food by sterilization. This historical sketch although condensed, is highly valuable and presents in small space the most important points in the history of the subject. The four principal methods of food preservation are treated in the following order. The first, sterilization

by heat, extends from p. 64 to p. 231, inclusive. The various technical processes which have been employed are set forth at length, and the directions for the preparing of foods for sterilization are particularly valuable, and are given in detail for all foods of every description. The conservation of foods by cold is the second method treated, from p. 232 to p. 320 inclusive, and modern methods of refrigeration are fully described. The third section is devoted to the conservation of food by desiccation, and extends from p. 321 to p. 427, inclusive. In the methods of drying foods the most modern processes which have been so successfully applied in the case of eggs and milk are not described. These processes were probably not patented in time to be brought to the notice of the author. They consist in injecting the milk or egg in the form of a spray into a large, dry chamber of such a magnitude and kept at such a temperature, that the minute particles of the spray become almost instantly desiccated and fall to the bottom of the chamber in the condition of fine, dry powder. A remarkable point in desiccation of this kind is that the albumen both of the milk and egg, although subjected to a temperature high enough to coagulate it completely under ordinary conditions, remains entirely soluble when dried in this instantaneous manner.

The most important section of the work at the present time is the fourth, devoted to the preservation of food by antiseptics, extending from p. 428 to the end of the work. The author states that in regard to the use of antiseptics for the preservation of food, the greater number of savants and hygienists have expressed themselves as opposed to their employment, while a smaller number favor their toleration in certain minimum quantities. Pasteur is quoted as saying, in 1891, that he advocated a tolerance of them, on condition that the manufacturers make known the nature and quantities of the substances employed. The author sums up the matter by saying that tolerance towards antiseptics has met with only a few partisans among hygienists. The Consulting Committee of Hygiene and the Council of Hygiene have successively condemned the employment of antiseptics. The Congress of Medicine, which was held in 1900, acting on a report made by MM. Brouardel and Pouchet, adopted the following resolution :

“In view of the many injuries pointed out by the authorities in different countries, resulting from the habitual use of foods and drinks preserved with chemical substances, the employment of these substances, namely, borax, salicylic acid,

saccharin and formaldehyde, in food materials, should be prohibited."

The author concludes, from a study of all the literature available, that it seems rational to prohibit, in a general manner, the use of antiseptics in food products, for if a large tolerance in regard to their employment were to be permitted we should absorb daily large quantities of drugs in our food, and this would assuredly be attended, in many cases, with unpleasant and serious consequences.

In regard to sulphurous acid, however, the author remarks that its use has been established by long practice and that it is the only antiseptic whose employment should be regarded as legitimate. It appears, in this respect, that the author has been influenced by the necessities of commerce in his country, and if sulphurous acid is to be permitted for this reason, there is no other antiseptic which will fail to find a like puissant champion, in some country or other.

The author concludes with a description of the different technical methods attending the use of antiseptics, all of which, however, are condemned with the exception of sulphurous acid.

This book will be found useful to all classes of chemists, food inspectors and those engaged in the technical processes pertaining to the preservation of foods.

H. W. WILEY.

THE BECQUEREL RAYS AND THE PROPERTIES OF RADIUM. By HON. R. J. STRUTT, F. R. S., Fellow of Trinity College, Cambridge. Second Edition. New York: Longmans, Green & Co. London: Edward Arnold. 1906. pp. 215. Price, \$2.40 net.

The appearance of the first edition of this book has already been noted in this JOURNAL.¹ It will, therefore, be sufficient simply to call attention to the fact that a second edition has been called for in such a short time. In the words of the author "This edition has been brought up to date, while some discussions of points doubtful at the time the first edition was published, but now settled, have been omitted."

The comparatively large demand for the book would show that it has met a want.

H. C. J.

LEHRBUCH DER ANORGANISCHEN CHEMIE, von PROF. DR. H. ERDMANN, Direktor des Anorganisch-chemischen Instituts der königlichen technischen Hochschule zu Berlin. Vierte Auflage. Mit 303 Abbildungen, 95 Tabellen, einer Rechentafel und farbigen Tafeln. Braunschweig: F. Vieweg und Sohn. 1906. pp. 796. Price, M. 16.

The fourth edition of Erdmann's Inorganic Chemistry shows

¹ THIS JOURNAL, 33, 609 (1905).

thorough revision; it is enlarged from 757 pages to 796; the illustrations are increased from 287 to 303 and a new colored spectrum table—the absorption spectra of the rare earths—is added. Among additions to the text, 3 pages on radium, Van't Hoff's sequence of crystallization of the Stassfurt salts, and Birkeland and Eyde's calcium nitrate process are noticeable and illustrate Erdmann's care to give the latest results of scientific research, and to describe the newest technical processes which have proved, or are likely to prove, commercially profitable.

Erdmann is a chemist of the school which does not favor the introduction of physical chemistry into a text-book of inorganic chemistry. Few modern chemists agree with him. In this edition he has shifted the pages on "Electro-chemie" from the last chapter to a more suitable position in the introductory chapter on general chemistry.

In the review of the second edition of this book by Prof. Richards,¹ the faults of the book—mainly due to Erdmann's attitude toward physical chemistry—are clearly indicated. Yet it must be remembered that "Erdmann," while not too large for study, is the completest, best illustrated, modern, *descriptive* chemistry published, and it should be specially noted that, until the publication last spring of Prof. Alexander Smith's book, all large text-books of inorganic chemistry, giving due attention to physical chemistry, were not only very deficient in descriptive and technical data, but the technical data given were too often obsolete. Hence the deserved popularity of Erdmann's work, as well for study as for ready reference.

E. R.

KURZES REPETITORIUM DER ORGANISCHEN CHEMIE. By DR. KURT DAMMANN. Freiburg im Breisgau: Herdersche Verlagsbuchhandlung. 1906. pp. xiv + 256. Price, \$1.25.

This little book is based on the author's manuscript notes, which he used for a number of years in the conduct of tutorial classes. The book itself is, of course, not intended to be employed as a text-book, but as a means of rapidly refreshing the memory and, more particularly, for the purpose of quickly preparing for an examination. Works of this class, though extremely plentiful in English, are rather scarce in German. Is the publication of the present one to be regarded as a sign that the examination epidemic, which has raged unchecked for so many years in Great Britain and China, has at last commenced to attack the German Empire? Germany's rivals will sincerely hope so!

¹ THIS JOURNAL, 25, 250.

Dr. Dammann's book is not suited for students who are beginning the study of organic chemistry, but those who have acquired some knowledge of the subject may find it useful for the purposes for which it is intended. The statements in the book are, in general, clear, concise and accurate, and the selection of material appears to have been, on the whole, judicious and careful.

J. B. T.

ELEMENTS OF GENERAL CHEMISTRY, WITH EXPERIMENTS. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Northwestern University Medical School. Fourth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. Price, \$5.00.

In the preface to this edition the author states that "some additions have been made in the presentation of chemical theory and in the description of new substances. Most of the added matter is given in a chapter not in the older editions, on the theories of solution and the conditions of chemical equilibrium."

This book is intended for freshman students of chemistry and is well adapted for the purpose. The author has avoided the very common mistake of introducing too much theory at this stage and has only given enough to make the experiments intelligible. The latter are well selected and clearly set forth; the descriptive part is concise and yet not lacking in important details. While there is no essential difference in the nature of the matter nor in the method of its presentation from other text-books of a similar grade, this book is as satisfactory as most of those in this field and may fill the need in some cases better than others of its kind.

J. E. G.

THE CYANIDE PROCESS. An Introduction to the Cyanide Process Including the Determination of the Applicability of the Process to an Arc. By ALFRED S. MILLER, formerly Professor of Mining, Metallurgy and Geology, University of Idaho. Second edition, revised and enlarged. New York: John Wiley & Sons. 1906. pp. 95. 28 Figures. Price, \$1.00.

The preface to this manual says: "This book was written primarily for the writer's students in doing laboratory work. The demand from most of the gold mining regions of the world for copies of this book has made it necessary to issue a second edition." "This book has not been written for the expert . . . but for the larger number of persons who have no knowledge of the subject."

The book is abundantly illustrated, the chemistry of the cyanide process and of its modifications is clearly explained, descriptions of the various patented processes are given, but the distinctive and essential value of the work lies in its simplicity

and clearness, enabling mining men with little knowledge of chemistry to understand the details of the process. E. R.

A LABORATORY HANDBOOK FOR THE ANALYSIS OF MILK, BUTTER AND CHEESE. By JAMES RITTENHOUSE EVANS, B.S. New York: Arthur M. Allen. 1906. pp. 60.

This small work of 60 pages contains schedules of the principal examinations of milk by approved methods. No attempt is made to enter into detail, or to explain the principles upon which the processes depend. The manual will be useful to chemists who are not accustomed to milk analysis and who do not wish to take the trouble to look through standard works for the occasional analyses required. In addition to milk analysis, there is a short chapter on the examination of cheese and a longer treatment of butter examination. In the appendices are found certain of the standards of purity for food products contained in circular No. 10 of the Office of the Secretary of Agriculture, but only in so far as these standards pertain to milk, butter fat, cream, butter and cheese. There is also appended a description of the Babcock method of determining fat in milk.

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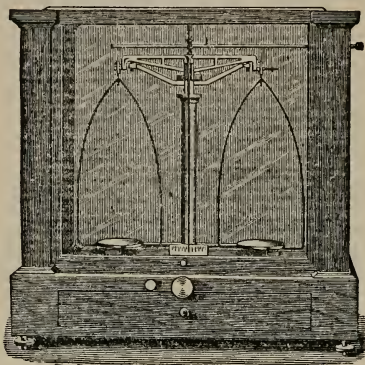
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4 XV.

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4 XVI.

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4 XVIII.

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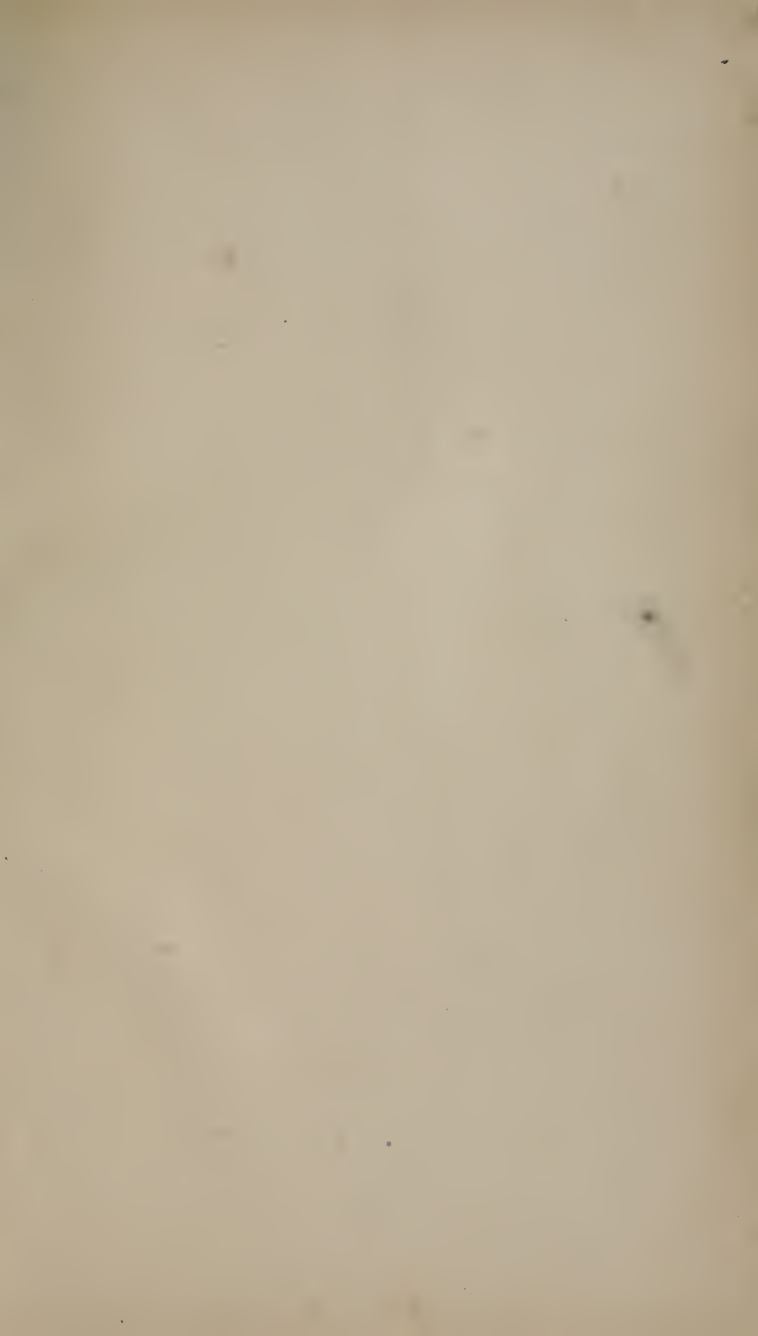
C₃₀-GROUP.

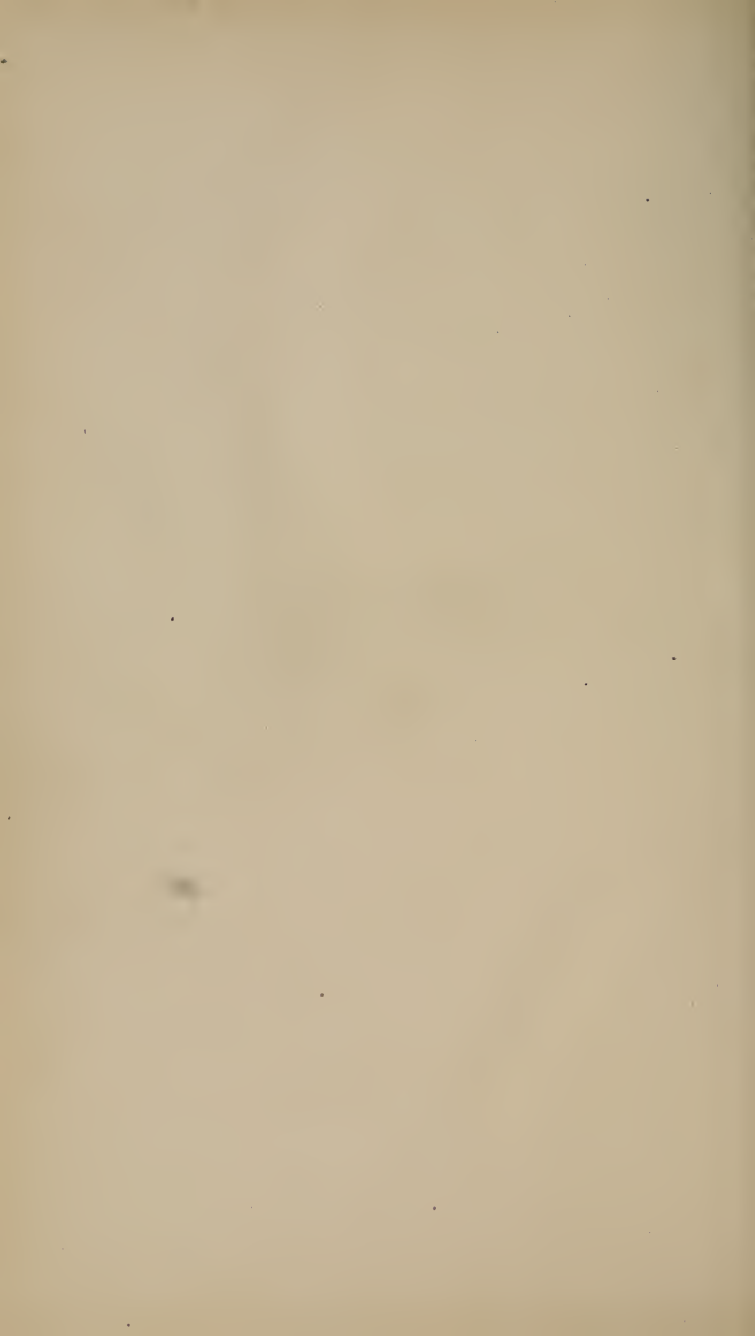
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ERRATA.

✓	Vol. 36, No. 3, Page 236, line 8,	¹ for	bicamphoformeneamine-carboxylic read biscamphoformeneaminecarboxylic.
✓	" " " 257, " 15,	¹ "	235° read 245°.
✓	" " " 261, " 6,	" "	into read in to.
✓	" " " 262, " 8,	¹ "	pyramidal read clinodome.
✓	" " " 263, " 1,	" "	16° read 19°.
✓	" " " 279, " 18,	" "	4506 read 4596.
✓	" " " 290, " 15,	" "	hydroxyacrylate read hydroxyacrylate.
✓	" " " 294, " 4,	¹ "	die read den.

¹ From foot.







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